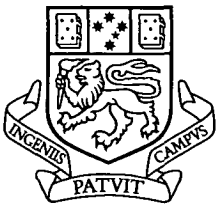
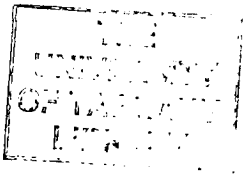


UNIVERSITY OF TASMANIA

THE SYNTHESIS OF ADSORBENTS FOR METAL IONS IN SOILS AND ORES

by

Andrew Clifton Grosse, B. Sc. (Hons.)



This thesis submitted in requirement for the degree of Master of Science at the University of Tasmania.

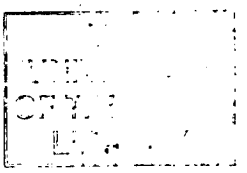
School of Chemistry,
University of Tasmania,
April 1998.

DECLARATION

To the best of my knowledge, this thesis contains no copy or paraphrase of any material previously published or written, except where due reference is made.

Andrew Grosse

Andrew C. Grosse



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A final note of thanks go to my wife Melysa
and my son Beowulf, both glad in the knowledge
that this thesis is now complete.

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ABSTRACT

A series of porous copolymer resins with ionogenic or chelating functional groups was prepared from commercial polystyrene or polymethacrylate precursors. Samples of all resins were supplied to Geo2 laboratories for assessment of their efficacy in a proprietary heavy metal remediation process. Two of these resins, DMA-1 and CMS-2, were prepared in bulk to supply pilot scale testing.

The crosslinked resin-bead substrates used were: chloromethylated polystyrene (CMS), diethylenetriamine poly(methacrylamide) (DMA), glycidyl methacrylate (GMA), and three types of poly(methyl methacrylate) (MMA, MMB & MMC) with varying degrees of porosity and crosslinking.

The alkyl halide moiety of CMS was used to anchor 2° or 3° alkylamines, diethylenetriamine, tris(2-aminoethylamine), or a quaternary ammonium group. Alternatively, a primary amine group was introduced via hydrolysis of hexamethylene tetramine.

Poly(ethylene glycol)s of various sizes were affixed to the chloromethylated substrate via Williamson ether synthesis to form "pseudocrown" ether chains. Benzocrown ether groups were produced by anchoring catechol to the CMS resin and subsequent reaction with α,ω-dichloropoly(ethylene glycol).

Functional groups on poly(methyl methacrylate) resins were introduced via hydrolysis of the backbone, or by aminolysis with tris(2-aminoethyl)amine or 2-aminoethanol. The epoxide moiety of GMA was

alkylated with either high-pressure ammonia, tris(2-aminoethyl)amine, or various grades of poly(ethylene glycol)s. Hydrolysis of the epoxide in aqueous acid was also investigated.

Resins with aminocarboxylate moieties were prepared via carboxymethylation of resins with primary amine or diethylenetriamine groups (including DMA), using excess chloroacetic acid in aqueous carbonate solution. The moieties prepared were diethylenetriamine triacetic- and tetraacetic- acids, and aminodiacetic acid. Several non-porous pseudocrown ether materials were also produced via copolymerisation, yielding urethane or methacrylate substrates.

The resins were characterised by elemental analysis, and by their Infra-Red spectra. A subset of resins was also characterised by their affinity and capacity to adsorb metal ions in aqueous solution. The sorption of copper from a 75 ppm solution into these resins was measured over a 25 hour period. Adsorption isotherms for Cu^{2+} in 0.010 M aqueous hydrochloric acid were also obtained in the range 10-75 ppm. The highest metal capacities were achieved with aminocarboxylate functionalities; amine resins adsorbed very little.

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1. INTRODUCTION

1.1 Heavy Metal Remediation

Heavy metals are often a hazardous and costly problem when diffused in ore, soil, or water [1]. Often quite valuable in a purer form, many metals (such as mercury, arsenic, lead and chromium) are highly toxic. Their diffusion into the ecosystem is almost always caused by human activity, such as mining or manufacturing. Areas with such environmental contamination are hazardous to wildlife, and of limited use for agriculture. Even the overabundance of less toxic metals, such as copper and zinc, can render a location uninhabitable. The remediation of toxic metal contaminated sites is a substantial ongoing cost to industry and government. Clean-up is required in regions such as mine tailings dams, ex-refinery sites, former paint factories, and livestock drench pits.

The amount of heavy metals in the soil of agricultural and residential land must be below environmental limits. Re-use of a contaminated site necessitates that these limits be met. Many techniques have been applied to remove heavy metal contamination from soil and water. The mobilisation of the metals from solids by leaching in aqueous solution is commonly employed, and the leach liquor processed separately. The original matter may be returned to the site when it has substantially reduced metal content [2]. If the removal of metal contamination from polluted areas can also incorporate the isolation of

saleable metals, the cost of the process may be ameliorated. This might be done using chelating or ion-exchange resins to strip the metals from the leach solution.

The leaching of metal-contaminated matter in an aqueous solution can release the metals as ions. The solubility of a metal is influenced by many factors, such as the concentration and type of counter-ions. A chelating agent may be used to replace or augment these counter-ions, to enhance mobilisation, or to precipitate the metals from solution. A chelating ion-exchange resin bears many chelating groups, anchored to a porous polymeric backbone. The metal-loaded resin may be physically separated from the leach liquor after chelation, and the metals removed as the resin is regenerated for re-use. The concentrated metal solution removed from the regenerated resin (strip liquor) may then be treated more economically. Most chelating structures show varying affinities for different metals. Exploiting this characteristic may introduce metal selectivity to an extraction process.

A series of chelating and ion-exchange resins was required for testing in a remediation process for a series of target metal ions from contaminated matter, under development by Geo2. These resins were developed to identify and optimise the chelating structures, polymer substrate, and resin bead characteristics to be used in pilot plant tests. Resin development was guided by feedback from the testing laboratories, optimising resin performance to the process conditions.

1.2 Ion-Exchange and Chelating Resins

1.2.1 Porous Copolymer Resins

Copolymer resins act as solid insoluble supports for functional groups in liquid and gaseous media. Columns filled with tightly packed beads of such material are often used as the stationary phase in liquid chromatography. Each spherical copolymer bead is a single porous macromolecule, with a high internal volume. Polymer chains made of a single repeating subunit (monomer) are held in place by covalently bonded bridges, or crosslinks. The large surface area that results, up to 500 m^2/gram, is mostly associated with a network of long, narrow channels ("pores") within each bead [3]. The size of the pores defines which ions and molecules have access to the inner surface. The large surface area permits a large number of functional groups to be available to a solution within the pores.

Non-polymeric substrates such as carbon, silica gel, zeolites, and minerals have been used for the processing of metal solutions. Unless the metal is quite valuable, such techniques are not often economical on a large scale. Although physically very sturdy, many of these substrates (such as silica gel with covalently affixed alkane groups) are not as chemically robust as copolymers. For example, silica gel is destroyed by hydrolysis when the operating pH is below 2 or above 12, whereas polystyrene backbones are robust in the pH range 0 to 14. Another

problem with inorganic substrates is the affinity of ions for the backbone, which can become "poisoned" with metal or organic matter and become useless. Mineral substrates such as zeolites usually have higher densities and correspondingly lower surface area per unit mass, hence relatively low capacities are observed. These, and materials such as carbon, cannot be selectively functionalised, and often cannot be regenerated economically. For these reasons, these substrates were deemed unsuitable for the Geo2 process.

1.2.2 Manufacture of Resin Substrates

The most common substrates used in crosslinked copolymer resins are polystyrene, and polyacrylates. Monomers such as styrene, acrylonitrile, and esters of acrylic or methacrylic acid have been used to prepare these resins, using crosslinking agents such as ethylene glycol dimethacrylate or divinylbenzene. Styrenic and acrylic resin beads are formed in similar fashion, via suspension polymerisation. Radical copolymerisation is initiated between the monomer, such as styrene, and a crosslinking agent, such as divinylbenzene (DVB), suspended in rapidly stirred aqueous media.

Surface tension effects generate viscous droplets of polymerising organic components, which remain tiny due to the shear forces of rapid agitation. The formation of insoluble beads is initiated by the branching of growing polymer chains with the more reactive crosslinking agent. These

core beads become sites of further polymerisation as the organic component of the reaction system becomes attracted to the more hydrophobic polymer surface. Polymerisation proceeds with a decreasing degree of crosslinking, and the formation of pores between the polymer strands. The final product is given rigidity by the many layers of polymer strands, all confined by crosslinking. Acrylic backbones are known to be more elastic than polystyrene, due to the higher steric hindrance of the aryl groups in a polystyrene chain [4].

The average dimensions and abundance of the pores are parameters that depend upon reaction conditions [5]. Empirical relationships have been established for specific reaction systems, with key variables being the reaction temperature, concentration of the catalyst, the ratio of monomer to crosslinking agent, and their concentrations and relative reactivity. Further enhancement with surfactants, co-solvents, salts and other additives is common practice. In particular, carefully selected diluents, or "porogens", can induce the formation of a network of permanent pores with a narrow size distribution [3]. The stirring speed and the dimensions of the reaction vessel are influential on the resulting particle size. The product beads vary in size in a Gaussian distribution, although limitations in the synthesis procedure give a maximum bead size of approximately 2000 μm. The most critical factor is the proportion of crosslinking agent incorporated into the matrix, which influences the particle size, porosity, and rigidity.

1.2.3 Resin Pore Structure

The porosity of a bead characterises its mechanical strength, swelling, and the kinetics of interactions with internal functional groups. Resin porosity is loosely divided into two categories; lightly crosslinked *microporous*, or "gel" substrates, and heavily crosslinked *macroporous* copolymers. The macroporous resins (up to 60% crosslinking) have large, rigid pores (ca. 1000 nm), whereas microporous resins commonly incorporate less than 5% crosslinking agent by weight, and their pores are small, flexible and impermanent. These micropores (ca. 50 nm) are created by the adsorption and diffusion of solvent between polymer strands, producing a viscous interphase. The most obvious effect of this differentiation is that large ions will not readily penetrate a gel copolymer, yet diffuse easily in a macroporous network. Microporous resins are also capable of bearing a high loading of functional groups, due to the inherent flexibility of the pore network. However, the rigid, spacious network of a functionalised macroporous resin permits fixed regions of high charge density, enhancing ion affinity. Macroporous resins are often also isoporous, ie. secondary crosslinking is introduced in the pore structure, increasing rigidity. The formation of methylene bridges between aromatic groups during the chloromethylation of polystyrene is an example.

As is the case with inorganic substrates, copolymer resins are susceptible to fouling by complex high-molecular weight ions. This can occur via ion-exchange, and by lipophilic (Van der Waals) interactions

with organic contaminants. The pores become clogged, and ionogenic groups are masked by contaminants. Rigid, highly crosslinked substrates with large inflexible pores have been reported to minimise these effects for organic soil components, such as humic and fulvic acids [4].

The *water content* of a resin is a measure of the amount of water entrained within the pores of a sample of resin, usually reported as a percentage (Table 1.1). Lightly crosslinked matrices may consist of over 75% water in fully hydrated form, decreasing with increasing crosslinking. Resins usually swell in volume when hydrated, although unmodified resin backbones often have a poor affinity for water. As hydrophilic (water-attracting) functional groups are introduced, the water content of the resin can rise. This results from the hydration of fixed ionogenic groups and their counterions, and electrostatic repulsion of like charges [6]. Reversible volume changes also occur in wet resins when the external pH varies, and when ions are adsorbed. Osmotic equilibrium between the hydration forces of the ionogenic polymer matrix and the restraining crosslinks determines the final bead volume and water content. The degree of swelling possible is inversely proportional to the degree of crosslinking [4].

The degree to which a polymer resin will swell in a favourable solvent depends upon the degree of crosslinking, the crosslinking agent, and the porosity achieved during synthesis. A resin will swell more if there is a low degree of crosslinking, a long and flexible crosslinking

agent, and there are abundant large pores. Most resins will swell considerably more in an organic solvent than in aqueous solution, as the former can soften and solubilise some of the polymer matrix. A good solvent for the linear polymer is generally a good swelling agent for the crosslinked substrate. Resin substrates, including methacrylate esters, are relatively hydrophobic, but will permit the absorption of large amounts of swelling solvent. The enlargement of the resin in swelling solvents is advantageous in functionalisation reactions, although some moieties are introduced in sites that are not accessible to aqueous solution.

Resin & Substrate	Moiety/Form	% Water	DWC (meq/g)
C100 (PS-Gel)	Strong Acid (Na^+)	44-48	4.6
C160 (PS-Mac)	Strong Acid (Na^+)	35-40	4.6
C105 (AC-Gel)	Weak Acid (H^+)	43-48	10
C106 (AC-Mac)	Weak Acid (H^+)	52-58	8.3
A400 (PS-Gel)	Strong Base (Cl^-)	48-54	3.8
A500 (PS-Mac)	Strong Base (Cl^-)	53-58	3.8
A850 (PS-Gel)	Strong Base (Cl^-)	57-62	4.4
A860 (PS-Mac)	Strong Base (Cl^-)	66-72	3.7
A100 (PS-Mac)	Weak Base (FB)	53-60	4.5
A830 (AC-Gel)	Weak Base (FB)	47-53	7.6
A835 (AC-Mac)	Weak Base (FB)	65-73	4.9

Table 1.1 Table of DWC and %Water for Purolite Resins [7]

(Resin Substrates: AC = polyacrylate; PS = polystyrene)

(Resin Porosity: Gel = microporous; Mac = macroporous)

(DWC: Dry Weight Capacity, calculated from bed capacity)

To obtain a resin in an anhydrous state, it must be heated in air at 105°C, or in a vacuum oven at 60-80°C, for several hours. While acrylic and polystyrene resins are stable to over 200°C, many functional groups anchored to the substrate are susceptible to thermal degradation at temperatures above 60-120°C [3]. Functionalised microporous beads are more resistant to thermal degradation, possibly due to the low glass-transition temperature. A polymer matrix can also be damaged by rapid changes in temperature, to which macroporous resins are more resilient. Most commercial resins are supplied with a summary of the bead characteristics such as maximum operating temperature, optimum operating conditions, porosity, size distribution, water content and capacity.

1.2.4 Ion-Exchange and Chelation

The abundance of functional groups of a macroporous copolymer resin is measured by its *capacity*, in milli-equivalents of functional group per gram of resin. This can vary according to the ionic form, such as between a free amine and an ammonium salt. The water content of the resin also influences the capacity, acting as a diluent. Hence, the functional group loading of a resin in an anhydrous state, or *dry weight capacity* (DWC), is used. The wet resin is forced into a known ionic form, generally by strong acid or strong base, and dried in air or vacuo (depending on the sensitivity of the functional group). Absolute capacity can often be determined by elemental analysis, although the effective

capacity can only be determined by intensive techniques, such as titration, or the determination of resin-metal ion isotherms.

When a resin is hydrated, the ionogenic functional groups usually dissociate to yield a fixed ion and a solubilised counterion. Strong acids and bases dissociate fully between pH 1-14, whereas a weak acid or base shows an equilibrium between the molecular and ionised forms. Weak (carboxylic) acids can be effectively characterised by their pK_a, defined as follows:

$$pK_a = -\log K_a, \text{ where } K_a = [RCOO^-].[H^+]/[RCOOH].$$

Analogous conditions apply for weak bases (amines):

$$pK_a = -\log K_a, \text{ where } K_a = [R_3N].[H^+]/[R_3NH^+]$$

The heterogeneous structure and moiety distribution of a copolymer substrate cause localised variations of charge density, and hence a narrowly distributed range of pK_a values is observed.

Metal ions may be stripped from aqueous solution by the action of chelating resins. As the leach liquor diffuses into the pores, the abundant chelating groups anchored within the resin entrap metal ions, until the action of counterions dislodges them. A chelating group by definition has a strongly favourable equilibrium with the metal ion, and will resist exchange with less favourable ions. Desorption of the metal and regeneration of the resin requires alteration of the equilibrium, usually by adding lixiviants or changing the pH of the aqueous phase. Leaching of the resin in a strong mineral acid solution ($pH \leq 0$) is commonly

employed. In acid stripping, the abundant hydronium ion (H_3O^+) displaces the metal ion, as the complementary anion replaces the resin chelating group. The strip liquor becomes a strongly acidic metal ion concentrate, from which metals may be isolated by precipitation or electrochemical methods.

Many chelating groups exhibit characteristics of acids and bases, ie. they are amphoteric. Ligands bearing carboxylic acid and amine groups, for example ethylenediamine tetra-acetic acid (EDTA), may act as a proton donor or a proton acceptor. This can present considerable difficulties when attempting to measure the effective capacity of a resin with such groups by titration. Regeneration of a strongly chelating resin may be complicated by amphoteric effects, or may even prove to be impossible. Useful moieties need to have a good affinity for the target metals, yet remain labile enough to permit stripping of the resin. A poor affinity with common cations such as calcium, sodium and magnesium is also desirable, as a significant background level of these ions is not uncommon.

Chelating groups, and other ligands, can be characterised by their equilibrium with hydrogen ions, or pK values. These are defined from the equilibria of the stepwise protonation of polydentate chelating groups, in similar fashion to pK_a values. For example, for a tris(alkyl)amine ligand (L):

$$pK_1 = -\log ([L].[H^+]/[HL^+]);$$

$$pK_2 = -\log ([HL^+].[H^+]/[H_2L^{2+}]),$$

and $$pK_3 = -\log ([H_2L^+].[H^+]/[H_3L^{3+}]).$$

Stepwise stability constants of equilibria between polydentate ligands and specific metal ions, defined in an analogous manner, can also be used to characterise these groups. However, this information is quite dependent on experimental conditions [8].

Ion-exchange is a more subtle effect than chelation. There are two main differences: the ionogenic groups are not good chelating groups at the pH used, so their interaction with counter-ions is relatively weak. Secondly, the competitive effects of other ions are critical to the process, causing differential elution of cations or anions. Ion-exchange resins are engineered for rapid kinetics, and consequently low ion-residence times. Passage of a solution through a fixed bed of resin is the optimal procedure, as ion migration times are derived from statistical differences in these ionic interactions.

Anion-exchange is conducted with resins bearing fixed cationic moieties; whereas cation-exchangers use negatively charged groups. It should be noted that the ion-exchange capacity of a functionalised resin is only appreciable when the groups are sufficiently ionised, especially relevant to weak-acid or weak-base moieties. The abundance of fixed ions within a functionalised polymer matrix significantly influences the

adsorption of ions into the resin. These ionogenic groups create an imbalance between the concentration of ions in the resin and the external solution. The thermodynamic tendency to dilute the phases to equal concentrations (the *Donnan* potential) produces *osmotic pressure*, which is greatest at low external ion concentrations.

The osmotic pressure varies according to external ion concentrations (including solution pH). Pressures in the region of 100 atmospheres are common in commercial resins, and increase with the degree of crosslinking [4]. This pressure can effect mechanical damage to the resin if the concentration of ions (especially H_3O^+) in solution changes rapidly. Fractures may develop within the structure, as the ionised structure struggles to achieve equilibrium, and the bead may even explode! This effect, know as *osmotic shock*, is reported to be less severe in the pores of a macroporous resin.

Oxidative decomposition of the crosslinking, a common mode of resin decomposition, can also be minimised in a macroporous network. Strong oxidising agents such as nitric acid, chromic acid, chlorate ions, halogens, and peroxides will attack divinylbenzene bridges. Some transition metal ions can catalyse similar reactions in the presence of oxygen [4], which could be problematic in the sorption of heavy metals. Metal-catalysed decomposition of the functional groups, co-precipitation or deposition of metals and insoluble salts on the resin can also diminish its efficacy.

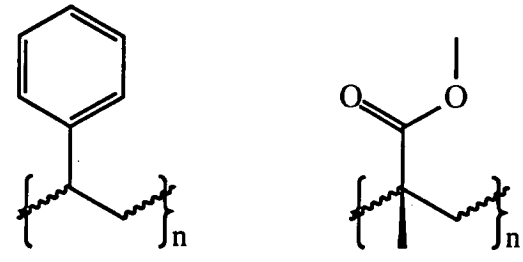
Heavy metals of interest to this process can be defined as the following set: arsenic, cadmium, chromium, copper, lead, mercury, nickel, tin, zinc, and radioactive metals. These metals are quite varied in character, and can be expected to show significant differences in mobilisation, loading onto, and stripping from the resins. Application of such a functionalised resin to leach liquor will concentrate the metal(s) in the aqueous phase within the resin. A large body of highly functionalised material can adsorb a significant proportion of available metals. If the substrate is robust to operating conditions, and can be stripped and regenerated economically, then the remediation of heavy metal contamination can be achieved with these resins.

1.3 Synthesis of Functionalised Polymers

1.3.1 Selection of Polymer Substrates

The functionalised polymers made for this project were generally prepared from a set of commercial precursor resins, and subsequently chemically modified. The use of ready-made porous bead substrates permits rapid synthesis of test materials, with similar structural characteristics (e.g. porosity, bead size). Precursor substrates were chosen with physical characteristics suitable for the Geo2 process, and amenable to subsequent chemical modification.

The substrates used for the resins prepared and supplied to Geo2 were selected within the following constraints, set by the parameters of a proprietary process. Large spherical porous copolymer beads of moderate density and high capacity were needed for lab-scale tests, in batches of 50-100 mL. Resin beads were selected for an optimal size of 600-800 μm, to facilitate easy handling in separation processes. Two robust types of chemically inert, highly porous crosslinked resin backbones were selected for development: polystyrene, and poly(methyl methacrylate) (or PMMA), as illustrated in Fig. 1.1.



Polystyrene **PMMA**

Figure 1.1 Polystyrene and Poly(methyl methacrylate)

The resins need to be quite physically robust, with a good affinity for water. Both polystyrene and PMMA are suitable, as they are stable in aqueous media in the pH range 0-14, at temperatures below 80°C. It should be noted that functional groups anchored to these resins may be susceptible to hydrolysis, oxidation, or other forms of decomposition in less severe conditions. Whilst some gel methacrylate resins were investigated, much of the work was conducted with macroporous

substrates. Geo2 report that trials with macroporous resins showed more favourable kinetics in the diffusion of large ions than the analogous microporous resins. Macroporous resins are also more resistant to osmotic shock [4, 6], which may facilitate more rapid metal stripping.

The preparation of resin beads via the copolymerisation of functionalised monomers was not investigated, due to the complex nature of suspension polymerisation. Instead, commercial substrates were obtained with functional groups susceptible to further derivatisation. These materials were subsequently functionalised by a variety of techniques. The manufacturers of these substrates will not usually divulge proprietary information, such as the type or percentage of crosslinking agent in the matrix. These precursor resins are characterised by factors such as pore size distribution, water content, network type (gel or macroporous), and the abundance of functional groups (capacity).

1.3.2 Commercial Precursor Resins

(i) Porous Methacrylic Copolymers

Purolite International (UK) have supplied three varieties of their poly(methyl methacrylate) based copolymer resins. The first of these, Purolite AC-6500 (MMA), is a lightly crosslinked gel copolymer with relatively low porosity. The beads were translucent pink to white, and approximately 500 μm in average diameter. Two macroporous copolymer resins were also supplied; Purolite D2844 (MMB), with an average particle

size of ~800 μm, and Purolite D2621 substrate (MMC), with a particle size of ~600 μm. Titrimetric analysis and control testing by Geo2 confirmed that the methacrylate precursor resins had negligible capacity.

An amide-amine functionalised resin, Purolite A-830 (DMA), was also supplied (Table 1.1). The resin backbone is again poly(methyl methacrylate), with diethylenetriamine groups anchored to the substrate by a terminal primary amide link (Fig. 1.2). The large yellow gel beads were on average ~600 μm in diameter.

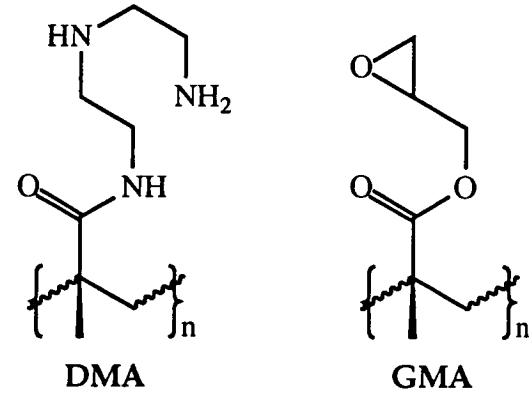


Figure 1.2 Diethylenetriamine Poly(methacrylamide) & Poly(2,3-epoxypropyl methacrylate).

Melcor Technologies (USA) have provided two batches of GM-300 glycidyl methacrylate copolymer beads for research purposes. The first batch supplied was of a widely varied size distribution (200-600 μm, GMA), and a second batch of larger beads (~800 μm, GMB) was later provided. Although less physically robust than PMMA substrates, the backbone

anchors more reactive 2,3-epoxypropyl ester groups (Fig. 1.2) and permits the substrate to be functionalised with a range of nucleophiles. Treatment of this resin with amines and alcohols should allow a comparison with similar moieties on polystyrene resins. Physical characteristics of the methacrylic precursor resins are summarised in Table 1.2.

Resin & Substrate	Moiety	Water %	DWC (meq/g)
MMA (AC-Gel)	methyl ester	19	~ 9.5
MMB (AC-Mac)	methyl ester	9	~ 9.5
MMC (AC-Mac)	methyl ester	9	~ 9.5
CMS (PS-Mac)	*p*-chloromethyl	25	~ 6.2
GMA (AC-Mac)	glycidyl ester	7	~ 6.7
GMB (AC-Mac)	glycidyl ester	11	~ 6.7

Table 1.2 Calculated Physical Characteristics of Precursor Resins

(Resin Substrates: AC = polyacrylate; PS = polystyrene)
(Resin Porosity: Gel = microporous; Mac = macroporous)

(ii) Porous Styrenic Copolymers

Several large batches of macroporous chloromethylated polystyrene (CMS) were supplied by Purolite, with average sizes of between 650-800 μm. These beads were prepared with the maximum capacity of chloromethyl groups possible, and contained small amounts of entrained synthesis residue. Soxhlet extraction with methanol removed ca. 2.0 g/L of yellow-brown organic residue. The earliest batches, denoted D-2780, were smaller in size (~650 μm). Later batches consisted of larger beads (ca. 800 μm), of which several hundred litres were supplied for bulk-scale

syntheses. Differences between these batches are responsible for the large variation in the abundance of chloromethyl groups (Table 1.2). Drying of this material at or above 80°C in air was observed to cause decomposition of the chloromethyl moiety.

(iii) Non-porous Acrylic Polymers

A batch of linear "thermoplastic" poly(methyl methacrylate), Oroglas V825, was obtained from AtoHaas, for the preparation of non porous functionalised analogues of PMMA resin substrates. This thermoplastic material (CMA) is expected to contain additives such as plasticisers (e.g. dioctyl phthalate) or UV-stabilisers. The distribution of polymer chain lengths was unknown, although precise values of a set of physical parameters was given: the specific gravity is 1.19 g/mL; water absorption after 24 hours immersion is 0.3 % by weight; and the glass transition temperature (T_g) is 109°C [9].

1.3.3 Target Functional Groups

Development of a viable chelating resin for the remediation of metal-rich liquors depends critically on the ligand structures used. Desirable functional groups for this process should have similar structures to the ligands which bind well with the target metals at the pH of the leach solution. These groups are reviewed in the following section, including a brief discussion of the likely interaction of a given moiety with aqueous metal ions.

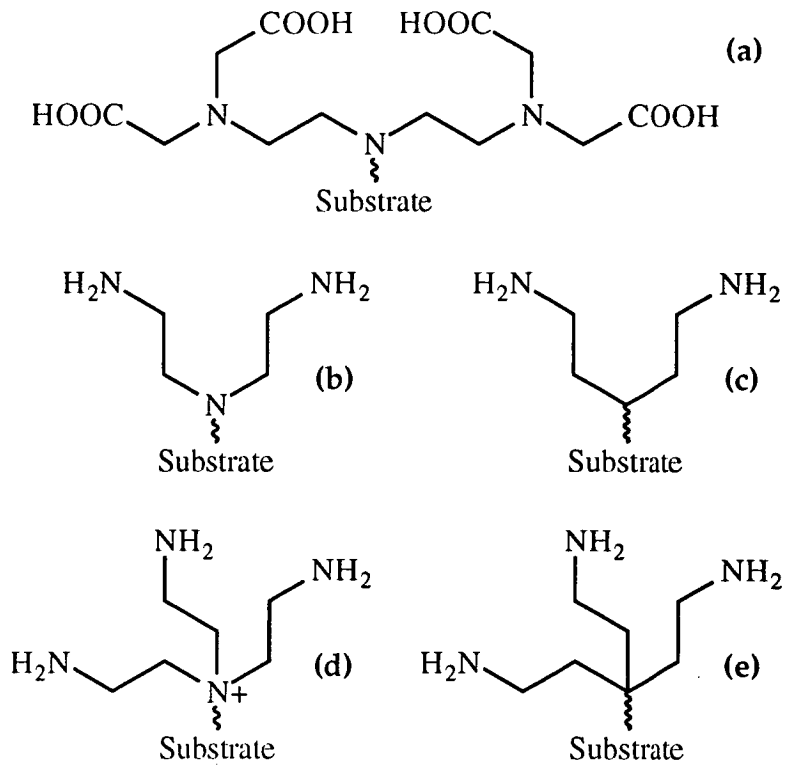
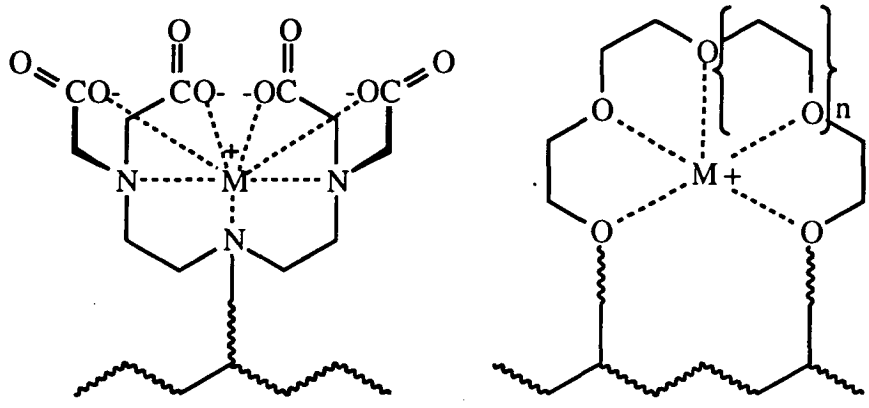


Figure 1.3 Target Chelating Structures (Geo2)

The initial aim of this project was to prepare resins with a series of alkylamine and aminocarboxylate moieties (Fig. 1.3). These structures are essentially variations of two key chelating moieties: tris(2-aminoethyl)amine, and diethylenetriamine penta-acetic acid (DTPA).

The first two moieties (Fig. 1.3 (a) and (b)) were readily prepared [10]; the others presented considerable difficulty and their investigation was deemed uneconomical. The initial set of functional groups to be examined was subsequently expanded to incorporate 1°, 2°, and 3° amines, carboxylic acids, and crown- and "pseudocrown"- ethers (Fig. 1.4). These

moieties were examined for heavy metal concentration effects, whether ion-exchange or chelation based.



Aminocarboxylate Chelating Group

Pseudocrown-ether Chelating Group

Figure 1.4 Chelating Groups on Arbitrary Metal (M^+)

The behaviour of a carboxylated substrate in comparison to a aminocarboxylate functionalised resins should illustrate the difference between ion-exchange and chelating resins. Weak acid cation-exchange resins usually bear only carboxylate groups, with pK_a values between 4-6, and are generally only useful when the solution pH exceeds the pK_a of the acid group. In ion-exchange conditions, they usually display an order of preferred affinity to given metal ions as follows: $H^+ \gg Cu^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Ca^{2+} > Mg^{2+} > Na^+ > K^+$ [4].

The development of "weak base" amine functionalised resins was conducted to differentiate the properties of 1°, 2°, and 3° amines in the process environment. The ion-exchange capacity of weak base resins is

significant only at low pH, when the amine groups become protonated. Conversely, the chelating effects of amines usually appear at high pH values, where they act as nucleophilic ligands. Variation of the length of the alkyl group between the polymer and the functional group ("spacer arm") [11] was not extensively investigated, as the high cost of such materials makes them unviable.

Crown-ethers are large heterocyclic structures consisting of oxygen atoms connected by short alkyl bridges. These flexible structures adopt low-energy configurations when an appropriate size cation is entrapped within the ring. Commonly, the ring is constructed of repeating units such as poly(ethylene glycol). If the ring contains an aromatic group, the compound is denoted a benzo-crown ether. Considerable ion selectivity has been demonstrated with both monomeric and polymeric crown-ether derivatives of various sizes [12-16].

1.3.4 Functionalisation Reactions

Several factors act as constraints on the number and kind of synthetic steps chosen. Maintenance of the resin backbone integrity, and porosity, necessitates careful treatment of the resin during, and between, reaction steps. As resin pores can become clogged by organic or inorganic residues, their extraction before treatment and use of the substrate is desirable. This kind of contamination (often present in commercial precursors) can also hinder reactions on the substrate, and introduce

unwanted side-reactions. The final porosity achieved in a functionalised resin can also vary from that of the precursor through changes in the water content (swelling), or collapse of the matrix. For example, bead cellulose substrates are particularly sensitive to the presence and nature of solvent, and can permanently lose some or all porosity on drying, or after contact with an unfavourable solvent. Side-reactions that introduce crosslinking can also be detrimental to the porosity of a copolymer matrix.

The methods used in the preparation of functionalised resins can be somewhat arcane in nature, due the special synthesis requirements. Solvents and reagents used on polymer substrates need to be carefully selected to avoid damage to the resin and maximise conversion. Not only should crosslink degradation and additional crosslinking be prevented, but good resin swelling is needed for effective functionalisation. Similarly, multi-step syntheses need to utilise high-yielding reactions which minimise the formation of unwanted moieties. Residual functional groups from a prior synthetic step, or "print error", can be introduced by poor-yielding reactions. The timescale of reactions in porous resins is also enlarged to permit diffusion of the reagent(s) into the polymer matrix. Manufacturers usually have proprietary interests, sometimes in the form of patents, from the development of an arsenal of functionalisation reactions suitable for a given substrate. Published techniques used to prepare functionalised resins are often derived from this development. This project has been directed toward the development

of four types of moiety: carboxylic acids, alkylamines, aminocarboxylates, and crown-ethers.

(i) Carboxylic Acids

Carboxylic acid groups may be introduced to crosslinked polystyrene via Friedel-Crafts acetylation and subsequent oxidation with basic permanganate solution [17]. The unfavourable confined conditions for the acylation and oxidation give a low-capacity product with sparse *p*-carboxyaryl groups. Bromination, lithiation and subsequent reaction with CO_2 has also been reported to provide moderate capacity carboxylated polystyrene [18].

Carboxylated substrates have also been prepared from the hydrolysis of an alkyl ester substrate, such as methyl methacrylate, by the action of NaOH, KOH, or potassium superoxide in aqueous media, and by lithium iodide or *p*-toluenesulfonic acid in organic solvent [19-20]. This produces carboxylate groups anchored to the alkyl backbone, although hydrolysis of ester crosslinks may also occur. Such materials can be prepared with dry-weight capacities over 10 meq/g [4, 7]. Hydrolysis of GMA and GMB substrates can be tailored to minimise hydrolysis of the ester, and open the epoxy ring instead to give hydrophilic 2,3-dihydroxypropyl ester groups [21].

(ii) Alkylamines

The chloromethylation of a polystyrene resin allows subsequent introduction of a wide variety of functional groups. Unsurprisingly, many ion-exchange resins are prepared by simple substitution of the halogen of the chloromethyl group with an amine. This favourable high-yielding reaction takes place at or above room temperature to give weak base (1-3° amine) or strong base (quaternary ammonium) anion-exchange resins. The high reactivity of the *p*-chloromethylstyrene group is analogous to that of benzyl chloride, utilised in the preparation of quaternary alkylammonium salts as "phase transfer catalysts". As with ammonium salts, the analogous resins are most stable in chloride salt form. In hydroxide form, they are susceptible to decomposition by the elimination of an amine, or an alcohol (Hoffman degradation) [4]. Analogous resins prepared from n-(2-hydroxyethyl)amine (n=1-3) are often termed Type II resins. They show improved hydrophilicity, but are more prone to thermal degradation [4-7].

A primary amine can be introduced to CMS by reaction with aqueous or gaseous ammonia, although this can also introduce crosslinking via successive alkylation with neighbouring chloromethyl groups. This also reduces the number of 1°-amines present, giving 2° and 3° amines, and quaternary ammonium salts. Anchoring hexamine to the substrate, and subsequent acid hydrolysis, can avoid these side-reactions to yield only primary aminomethyl(polystyrene) [22-23]. The Gabriel reaction of potassium phthalimide with CMS, or direct imidomethylation of

crosslinked polystyrene via N-halomethylphthalimide, and subsequent hydrazinolysis to remove the phthalate protective groups, both introduce *p*-aminomethyl(aryl) groups [24].

The anchoring of an amine group on a methacrylic substrate presents more difficulty. The ester groups of a methacrylate resin can be substituted by other alcohols or amines under favourable conditions. This transesterification (alcoholysis) or transamidation (aminolysis) can be effected by swelling the resin in an excess of the alcohol (or amine) at a suitably elevated temperature [25]. It has been reported that the use of 2-aminoethanol on PMMA in such conditions yields a 19:1 ratio of amide to ester [26]. The reaction of PMMA resins with excess diethylenetriamine at 160°C is known to preferentially affix one primary amine tail, leaving a 1°-amine and 2°-amine group (Fig. 1.2). The transesterification of linear PMMA with branched polyamines, e.g. tris(2-aminoethyl)amine, may also introduce crosslinking to the structure.

Ammonia, 1°- and 2°-amines can readily be anchored to an epoxide group, such as that of GMA, by nucleophilic addition at the terminal carbon [27]. This reaction takes place at moderate temperatures, to avoid transesterification. This ring-opening reaction results in the formation of an α- hydroxyl group, which may enhance hydrophilicity and complicate the action of the amine group.

(iii) Aminocarboxylate Chelating Groups

Several varieties of resin with iminodiacetic acid functional groups {-N($CH_2COOH)_2$} are available commercially, and a wide variety of aminocarboxylate resins are reported in the literature [28]. The preparation of an aminocarboxylate resin based on diethylenetriamine has been reported, anchored to the resin by the central nitrogen and bearing four carboxymethyl groups [10]. The last stage of this procedure, the carboxymethylation of primary and secondary amines with 2-chloroacetic acid in aqueous carbonate, may be utilised to prepare chelating resins from other amine-bearing substrates.

(iv) Crown & Pseudocrown Ethers

Extensive literature also exists regarding the synthesis and use of copolymerised benzocrown-ethers and related compounds to form granular column packing material [12, 15, 16, 29]. These condensation polymers have low porosity and high cost, but show wide variations in selectivity due to crown size and structure [30]. Catechol has been anchored to chloromethylated polystyrene and alkylated with dichloro-terminated poly(ethylene glycol) in butanol to give varying sizes of benzocrown groups [31]. Crown- or benzocrown-ethers with functionalised substituents have also been used to anchor macrocyclic ethers to functionalised polystyrene [32].

When both ends of a polyether chain are anchored to a polymer substrate, it forms a crown-ether ring with an alkyl component of variable

size and conformation. Ring size and flexibility is determined by the distance between the random anchoring points, as in Figure 1.4. Warshawsky has denoted these functional groups "pseudocrown ethers". These can be prepared by Williamson ether synthesis using poly(ethylene glycol)s and chloromethylated polystyrene resin in dioxane [33]. It has been reported that these resins exhibit thermal decomplexation properties in methanolic solution [34].

Epoxides also undergo nucleophilic substitution and ring-opening with alcohols, albeit less energetically than amines. The reaction of a poly(ethylene glycol) with an epoxide may be used to prepare analogous pseudocrown materials with the GMA and GMB substrates.

Finally, the preparation of non-porous pseudocrown-functionalised substrates was also investigated. Modification of linear polymers via transesterification is well known, such as with ethylene glycol in the recycling of polyethylene terephthalate (PET). Transesterification of linear PMMA with PEGs should produce a crosslinked solid with abundant PEG-ester groups. Copolymerisation of functional monomers to construct functionalised polymers is also of interest. The neat polymerisation of poly(ethylene glycol)-400 dimethacrylate (PEG-400-DMA) should provide maximal loading of PEG-400 pseudocrown groups on an acrylic matrix. Alternatively, the two-stage reaction of toluene-2,4-diisocyanate with anhydrous PEGs may provide pseudocrown groups on an aromatic polyurethane matrix. These

materials are likely to be of low capacity, but should be more physically robust than porous materials.

1.3.5 Summary of Objectives

The principal aims of this project were to prepare (and characterise) high capacity functionalised resins from inert precursor beads, where the affixed functional groups fall into four categories:

(i) **carboxylic acids**

(ii) **alkylamines**

(iii) **aminocarboxylic acids**

(iv) **crown- and pseudo-crown ethers**

In addition to this, a series of resins was prepared as a control group, to permit the evaluation of side-reactions in synthesis. Several non-porous materials were also prepared with the intention of producing more robust functionalised substrates, but with necessarily lower capacities. Evaluation and comparison of the behaviour of each resin in the Geo2 process environment should then establish the desirable characteristics, yielding materials that give maximal performance in heavy metal remediation.

2. ANALYSIS OF FUNCTIONAL POLYMERS

2.1. Functionalised Resin Products

The resins prepared for Geo2 can be placed in four categories, according to the functional groups present: resins with carboxylate groups alone, aminocarboxylate groups, alkylamines, and the macrocyclic crown- and pseudocrown-ethers. Each resin was given a reference code of three letters denoting the substrate, and an identifying number; Appendix VI is a complete list of all resins prepared in this project. The behaviour of resins with comparable moieties but different substrates is of particular interest, as the chemical and physical structure of the polymer backbone may have substantial influence upon the efficiency of the resin [3, 4, 35].

The primary factor influencing the course of research was the assessment of each resin in the Geo2 heavy metal remediation process. This was conducted by the CSIRO Division of Minerals, or at Geo2 Laboratories, concurrent with optimisation of the process itself. Consequently, the characterisation data from this laboratory (derived from a reference portion of each resin retained) was supplementary in nature only. Resin mass in wet and anhydrous states gave the water content, whereas DWC (dry weight capacity) was evaluated from elemental analyses of anhydrous resins in known ionic form, or occasionally by titration (denoted tit^n). Some IR spectra were also obtained,

and a set of adsorption isotherms with aqueous Cu^{2+} at pH 2 were also developed for a subset of these resins.

2.1.1 Carboxylic Acid Groups

The most economical approach to high capacity carboxylate resins was the hydrolysis of an acrylic ester resin. Reaction conditions were altered to provide varying capacity, although the accompanying destruction of some crosslinking is believed to have occurred. The alkaline hydrolysis of two varieties of poly(methyl methacrylate) substrate permit some evaluation of their structural differences upon the degree and nature of hydrolysis. The carboxylate resins, prepared by aqueous alkaline hydrolysis, are detailed below, in Table 2.1.

Resin Code	Functional Group	DWC (meq/g)	% Water
MMA-2	carboxylic acid (H^+)	~ 1.3 (H^+) (tit^n)	n/a
MMA-3	carboxylic acid (H^+)	~ 7.5 (H^+)	60 (H^+)
MMB-2	carboxylic acid	n/a	71 (H^+)

Table 2.1 Resins with Carboxylic Acid Groups

2.1.2 Alkylamine or Polyamine Groups

Two types of amine-functionalised resins were produced: those with variations of tris(2-aminoethyl)amine moieties, and 1 - 4° ammonium salts on CMS. The tris(2-aminoethyl)amine groups were

anchored via formation of either a terminal amide, or alkylation of a terminal amine (Fig. 2.1). The second set of amine resins encompasses both type I (alkylamine) and type II (2-hydroxyalkylamine) moieties, with pendant alkyl groups up to C_8 in size.

The analytical data for the amine resins is collected in Table 2.2. Note that the capacity (DWC) is primarily based on elemental analysis, hence it does not discriminate between amides and amines (as in MMA-1, MMB-1, and MMC-1), nor discern the level of crosslinking via nearby chloromethyl groups in aminated CMS resins. The primary amine resins (CMS-2 and GMA-3) should be free from more highly substituted amines, due to the selective synthesis techniques used.

The tris(2-aminoethyl)amine resin MMA-1 contained a large proportion of distorted or fractured beads. This may have been an unfortunate side-effect of synthesis temperature exceeding the glass-transition temperature, collapsing some porosity permanently. Side-reactions forming bis- and tris-(amide) crosslinking may also create bead deformations. The observation that the number of damaged beads increased with use also showed the fragility of the high-capacity resin, especially with regard to osmotic shock (see Appendix II (e) and (f)).

The 2-aminoethanol affixed to resin MMA-4 was expected to be primarily anchored via an amide linkage, as the formation of an amide is more energetically favourable than an ester bond [26]. Some crosslinking

may also have been introduced by amide-ester formation. It was anticipated that a resin with a low capacity of 1°-amine groups may be prepared in this manner, allowing comparison between similar styrenic and methacrylic resins.

Resin Code	Functional Group	DWC (meq/g)	% Water
CMS-1	tris(2-aminoethyl)amine	1.36 (OH^-)	37 (H^+)
GMA-1	tris(2-aminoethyl)amine	1.58 (OH^-)	61 (H^+)
MMA-1	tris(2-aminoethyl)amine	2.95 (OH^-)	43 (H^+)
MMB-1	tris(2-aminoethyl)amine	0.34 (tit^n)	38 (OH^-)
MMC-1	tris(2-aminoethyl)amine	~nil	4 (OH^-)
CMA-1(a)	tris(2-aminoethyl)amine	0.08 (H^+) (tit^n)	73 (H^+)
CMA-1(b)	tris(2-aminoethyl)amine	0.08 (H^+) (tit^n)	72 (H^+)
CMS-2	1°-amine	3.51-4.87 (OH^-)	50 (H^+)
CMS-3	ethylamine	4.02 (OH^-)	40 (OH^-)
CMS-4	isopropylamine	4.63 (OH^-)	40 (OH^-)
CMS-20	triethylamine	2.45 (OH^-)	49 (OH^-)
CMS-21	diethylamine	2.84 (OH^-)	41 (OH^-)
CMS-22	bis(2-hydroxyethyl)amine	2.46 (OH^-)	38 (OH^-)
CMS-23	*n*-octylamine	2.00 (OH^-)	38 (OH^-)
CMS-24	benzylamine	2.57 (OH^-)	35 (OH^-)
CMS-25	2-hydroxyethylamine	2.73 (OH^-)	39 (OH^-)
CMS-26	butylamine	2.23 (OH^-)	36 (OH^-)
CMS-27	isopropylamine	2.56 (OH^-)	37 (OH^-)
GMA-3	1°-amine	n/a	64 (OH^-)
MMA-4	2-hydroxyethylamine	8.57 (OH^-)	44 (OH^-)

Table 2.2 Resins with Alkylamine or Polyamine Groups

(DWC results above derived from Elemental Analyses)

The copolymer resin CMA-1 was expected to contain internal crosslinking, via the formation of bis(amide) and tris(amide) bonds between the linear PMMA and the tris(2-aminoethyl)amine, as in Fig. 2.1. The two samples of hard yellow substrate were differentiated according to their solubility in tetrahydrofuran: CMA-1 (a) fully dissolved, whereas CMA-1 (b) softened but remained insoluble.

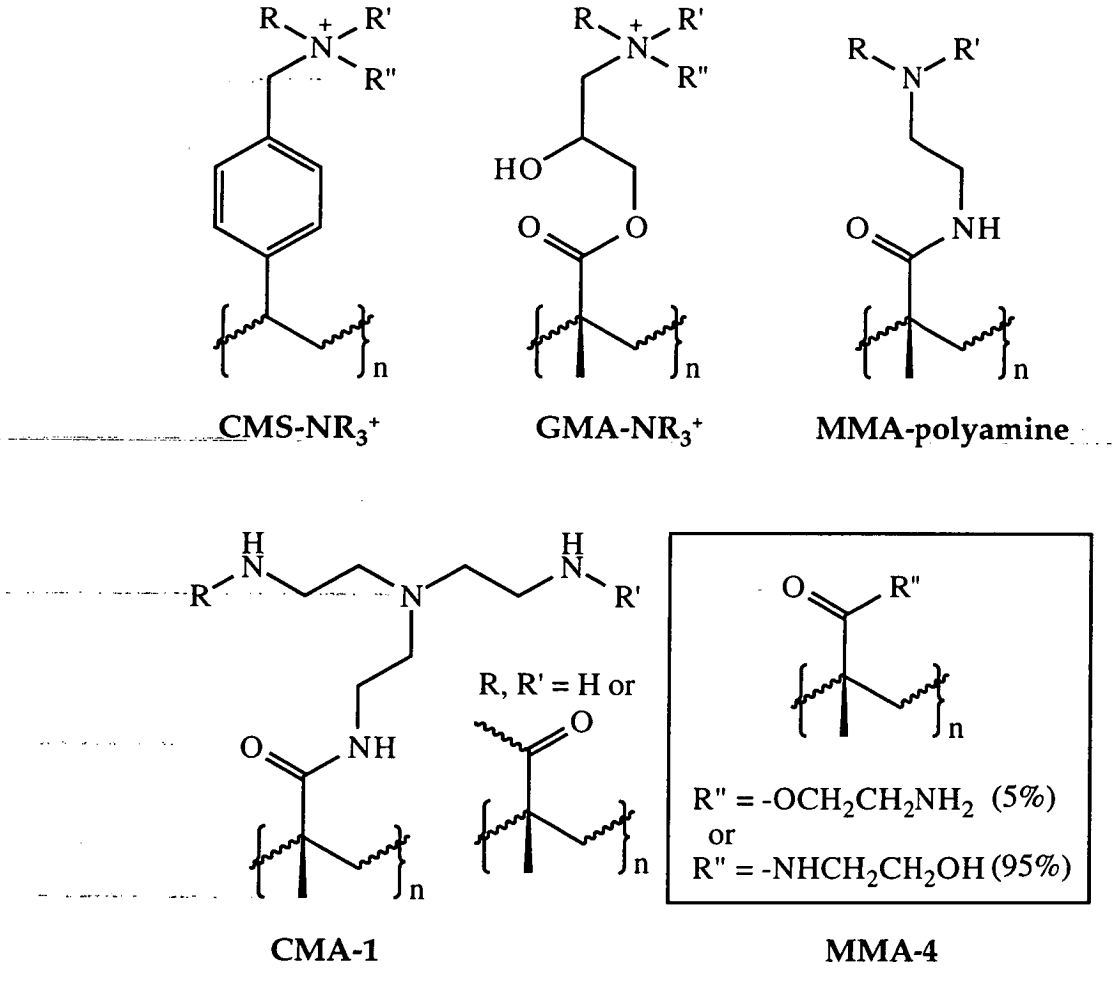


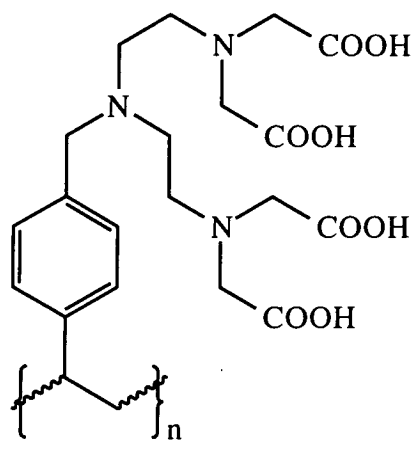
Figure 2.1 Structure of Amine Anchor Groups by Resin Type

2.1.3 Aminocarboxylic Acid Groups

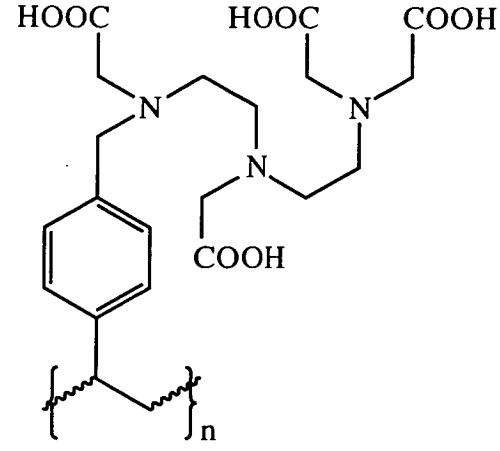
The aminocarboxylate bearing polymers collected in Table 2.3 were prepared via carboxymethylation of 1° and 2° amine-bearing precursors. Diethylenetriamine tetraacetic acid (DTTA) was anchored to CMS in two ways: symmetrically, via the central 2°-amine (*sym*-DTTA), or by a terminal 1°-amine (*asym*-DTTA). The latter method has been applied using methanol or 1,4-dioxane as swelling solvent. Alternatively, carboxymethylation of DMA affixes three acid groups, leaving the terminal amide nitrogen unmodified to yield diethylenetriamine triacetic acid (DT3A) (Fig. 2.2).

Resin Code	Functional Group	DWC (meq/g)	% Water
CMS-5	*sym*-DTTA	0.59 (H^+)	39 (H^+)
CMS-6	iminodiacetic acid	3.32 (H^+)	51 (H^+)
CMS-7	*asym*-DTTA	1.60 (H^+)	41 (H^+)
CMS-8	*asym*-DTTA	1.95 (H^+)	48 (H^+)
DMA-1	*asym*-DT3A	3.29 (H^+)	38 (H^+)

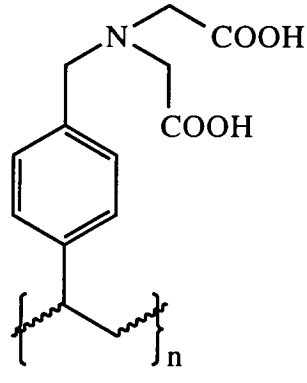
Table 2.3 Resins with Aminocarboxylic Acid Groups



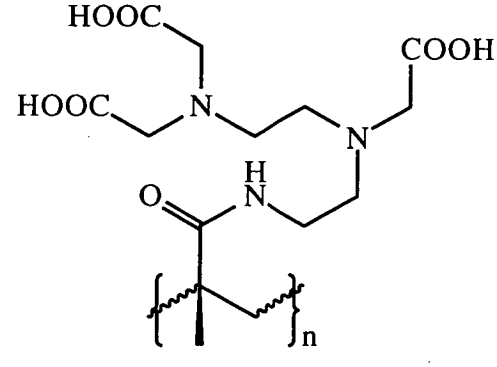
CMS-5 (*sym*-DTTA)



CMS-7,8 (*asym*-DTTA)



CMS-6 (iminodiacetate)



DMA-1 (DT3A)

Figure 2.2 Structure of Aminocarboxylate Groups

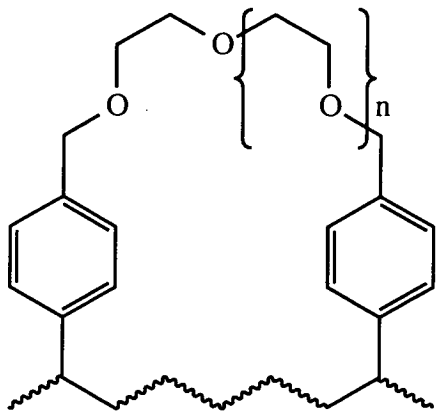
2.1.4 Crown- or Pseudocrown-Ether Groups

The macrocyclic ethers anchored to the substrates were derived from poly(ethylene glycol)s, or PEG, of various grades. Each grade consisted of a distribution of polymer chain lengths, with the average mass known (e.g. PEG-200 has a mean molecular mass of ~200). These were affixed by three methods: pseudocrown ethers on GMA and on CMS, and benzocrown ethers on CMS (Fig. 2.3). In each case, it was intended to

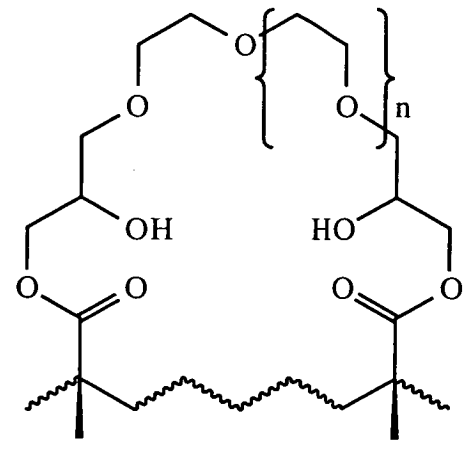
have both ends of the PEG chain anchored to the substrate, and hence obtain the analogous macrocyclic ring. Subsequent alkaline hydrolysis of resin GMA-6 was intended to enhance hydrophilicity.

Resin Code	Functional Group	DWC (meq/g)	% Water
CMS-10	benzocrown-400	0.13	37
CMS-11	benzocrown-600	0.025	37
CMS-12	pseudocrown-2000	< 0.01	35
CMS-13	pseudocrown-1500	< 0.01	35
CMS-14	pseudocrown-900	< 0.01	32
CMS-15	pseudocrown-600	< 0.01	32
CMS-16	pseudocrown-600	< 0.01	32
GMA-4	pseudocrown-900	0.26	59
GMA-5	pseudocrown-200	1.71	62
GMA-6	pseudocrown-900	n/a	68
GMA-7	pseudocrown-2000	n/a	65
GMA-8	pseudocrown-600	n/a	n/a
GMA-9	pseudocrown-400	n/a	65
GMB-1	pseudocrown-900	0.30	47
GMB-2	pseudocrown-400	n/a	41
GMB-3	pseudocrown-600	n/a	49
CMA-2	pseudocrown-400	1.76	24
CMA-3	pseudocrown-600	0.39	6.5
PUR-1	pseudocrown-600	0.98	31

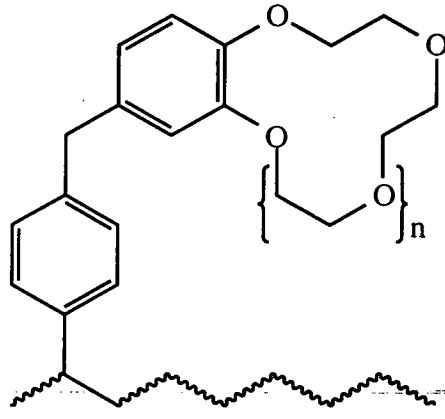
Table 2.4 Resins with Crown- or Pseudocrown-Ether Groups



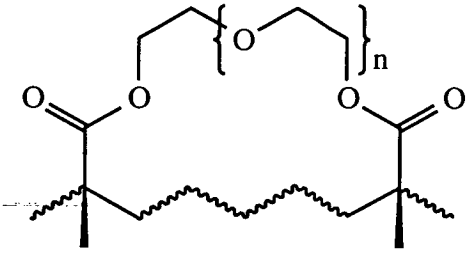
Pseudocrown Ether on CMS



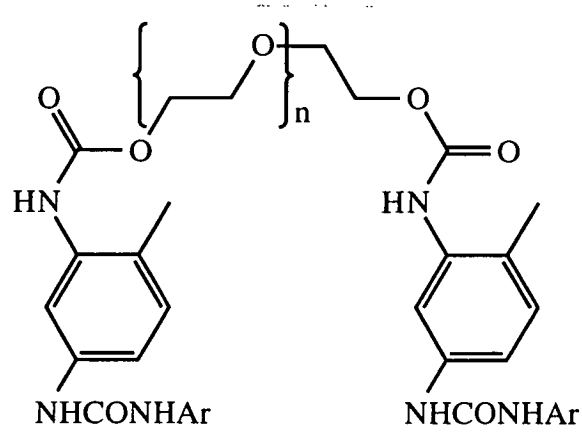
Pseudocrown Ether on GMA



Benzocrown Ether on CMS



CMA-2 (Polymeric Diacrylate)



PUR-1 (PEG-600 Polyurethane)

Figure 2.3 Structure of Ether Anchor Groups by Resin Type

Note that the last three resins in Table 2.4 (CMA-2, CMA-3 and PUR-1) are non-porous copolymerisation products. Resin CMA-2 is a brittle, translucent yellow solid composed of neat PEG-400 dimethacrylate, prepared by free-radical initiated polymerisation. The substrate CMS-3 is a hard transesterified polymeric alloy of PEG-600 and PMMA, catalysed with lithium iodide. The tough, flexible polyurethane product PUR-1 was prepared from a 'prepolymer' of PEG-600 end-capped with toluene 2,4-diisocyanate, and cured in moist air. Each of these anchor group types is illustrated in Fig. 2.3.

2.1.5 Precursor and Control Group Resins

These materials, summarised in Table 2.5, were prepared to establish that side-reactions do not become dominant in synthesis. This was of particular interest in the quenching stage of ether group synthesis, where excess sodium hydride is quenched with methanol. Thus, resins CMS-17 and CMS-18 were treated with sodium methoxide, in methanol and 1,4-dioxane respectively. Resin CMS-19 was prepared to study the effect of refluxing hydrochloric acid and methanol on CMS, which comprised the second step of the procedure used in the preparation of the primary amine resin CMS-2. Acid hydrolysis of the epoxide groups of GMA resin to the more hydrophilic 2,3-epoxypropyl ester was also investigated. This treatment was applied after reaction with PEG-900, to

enhance adsorption of water and solvated ions into the pseudocrown resin GMA-6.

Resin Code	Functional Group	DWC (meq/g)	% Water
CMS-9	catechol	2.43 (H^+)	39 (H^+)
CMS-17	chloromethyl	n/a	15
CMS-18	chloromethyl	n/a	29
CMS-19	chloromethyl	n/a	29
GMA-2	2,3-dihydroxypropyl	n/a	68

Table 2.5 Precursor and Control Group Resins

2.2 Characterisation Techniques

Quantitative and qualitative assessment of the abundance, environment and type of functional groups present was desired. The materials to be studied shared a set of characteristics which complicated their analysis. Most of the functional groups on the resin were within the beads, occluded by many external layers of copolymer backbone, which generally dominated any analytical spectra. This lack of homogeneity, and the porous, macromolecular nature of the substrates, precluded the use of common analytical techniques such as ultraviolet spectrometry, gas chromatography, and mass spectrometry. Similarly, whilst electron spectroscopy for chemical analysis (ESCA) can provide a chemical breakdown of the surface constituents of a sample, it cannot give useful

information about the interior of a porous particle [36]. Nuclear Magnetic Resonance (NMR) is known to have potential application in elucidating the internal structure of an organic copolymer matrix, but this technique was not readily applied to the present research. The direct characterisation techniques that remained were limited to the following options:

(i) **Elemental Analysis**

(ii) **Infra-Red Spectrometry**

(iii) **Gravimetric Analysis**

(iv) **Microphotography**

Indirect methods for study of the resin products could also be applied, although the results are very specific to the experimental conditions. These techniques are as follows:

(v) **Titration of Fixed Ionogenic Groups**

(vi) **Metal Ion Adsorption Isotherms**

(vii) **Remediation Tests (*in-situ* Application)**

2.2.1 Elemental Analysis (C, H, N)

The most direct means of assessing the number of functional groups in a fixed mass is the destructive chemical analysis of the anhydrous resin. The ionic from must be known, for it influences the mass of the anchored moiety, and thus the capacity of the resin. The

levels of carbon, nitrogen and hydrogen present in the sample are determined, and may be compared to the starting material. These methods were used to derive the reported DWC values in Tables 2.1 - 2.5, except where titration results were used (denoted by tit[n]).

Resin beads were analysed whole, after conversion to the appropriate ionic form, washing, and drying in a vacuum oven at 60°C. It is worth noting that the variation in elemental analysis from bead to bead may be as high as ± 0.3 %, depending upon the homogeneity of the substrate, derivatisation reaction, and drying process. Analysis of anhydrous pulverised samples may induce side reactions such as oxidation and quaternization, as the crosslinking would be destroyed.

For an ionogenic resin, the capacity (DWC) can be specified as the abundance of intact chelating moieties per unit mass. The capacities of amine resins are particularly easy to calculate from elemental analyses. Any and all nitrogen introduced to a hydrocarbon substrate must be associated with the added moiety. Thus:

DWC = [(%N / 100) / 14.0067] mol N per gram dry resin

= [(%N x 10) / 14.0067] milli-equivalents per gram (meq/g)

This formula was used to determine the capacities of the amine resins, without regard for the ligand structure. A complication in terminology occurs when polyamine ligands such as diethylenetriamine

or tris(2-aminoethyl)amine are anchored to a substrate. In this case, the ligand DWC can be derived by dividing the formula above by the number of nitrogen atoms in the ligand. Implicit in this derivation is the assumption that the ligand is anchored to the substrate by only one bond.

More complicated correlations need to be explored when calculating the capacity of a polymer with introduced functional groups that do not contain nitrogen. This applies to crown- and pseudocrown-ether materials, hydrolysed GMA and PMMA resins, and to the carboxymethylated derivatives of amine resins. Changes in the structure of the resin are reflected in variations in C, H, O, and N levels, and the degree of conversion can be elucidated from a linear graph of these elements between precursor and theoretical 100% yield figures. The proportion of a resin which is not carbon, hydrogen, or nitrogen is denoted 'other', and is generally composed of oxygen and chlorine. Theoretical elemental analyses, calculated for 100% conversion of all resin anchor groups to ligands, are given in Table 2.6. The amine resin was calculated as if in free-base form.

The elemental analyses of precursors (monomers and resins) given in Table 2.7 were compared to the theoretical values above. A set of estimates of % conversion was then made, which should be most reliable for the abundant elements. Complete conversion of all anchor groups was extremely unlikely, especially for large ligands such as PEG-2000 and tris(2-aminoethyl)amine. Additional complications arise when

considering a multistep synthesis, such as aminocarboxylate and benzocrown resins on CMS substrate. Each synthetic step achieves its own degree of completion, and each subsequent step must incorporate this limit into such calculations.

Resin & Affixed Moiety	% C	% H	% N	% other
CMS-diethylenetriamine	71.77	9.78	18.45	-
DMA-DT3A (3.Na^+)	43.30	4.88	9.84	41.98
CMS-catechol (2.H^+)	79.88	6.49	-	13.63
CMS-PEG(400) b.crown	66.97	8.00	-	25.03
CMS-PEG(600) b.crown	64.27	8.25	-	27.48
CMS-PEG(600) p.crown	64.16	8.69	-	27.15
CMS-PEG(900) p.crown	61.94	8.80	-	29.26
CMS-PEG(1500) p.crown	59.35	8.92	-	31.73
CMS-PEG(2000) p.crown	58.31	8.97	-	32.72
GMA-PEG(200) p.crown	54.75	8.22	-	37.03
GMA-PEG(400) p.crown	54.68	8.52	-	36.80
GMA-PEG(600) p.crown	54.64	8.67	-	36.69
GMA-PEG(900) p.crown	54.62	8.77	-	36.61
GMA-PEG(2000) p.crown	54.58	8.96	-	36.46
CMA-PEG(600) diester	54.95	8.45	-	36.60
GMA-hydrolysis (2.H^+)	51.79	7.88	-	40.33

Table 2.6 Theoretical Element Content of 100% Conversion

(b.crown = benzocrown ether; p.crown = pseudocrown ether)

In the case of simple CMS derivatives, the substitution of chlorine by hydrocarbons can also give an estimate of conversion, but must incorporate the mass of functional group introduced. Chlorine analysis

was not economical, hence linear elucidation of functional group conversion was attempted. The accuracy of this technique does not readily permit the evaluation of by-products, such as the proportion of PEG groups anchored by only one end. These differences cause only minor variations in the elemental abundances, and can only be assessed by more rigorous methods.

Monomer/Substrate	% C	% H	% N	% other
methyl methacrylate	59.98	8.05	-	31.96
MMA	58.53	7.63	-	33.84
methacrylic acid	55.81	7.02	-	37.17
PEG-400 dimethacrylate	55.11	8.18	-	36.71
PEG-600 dimethacrylate	54.95	8.45	-	36.60
p-chloromethylstyrene	65.38	7.05	-	27.57
CMS	71.66	6.33	-	22.01
glycidyl methacrylate	59.15	7.09	-	33.76
GMA	58.35	7.46	-	34.19
DMA (Free Base)	60.36	9.54	22.48	7.62

Table 2.7 Element Content of Monomers & Precursors

Due to the sheer volume of production (100 mL - 200 L), control samples were only obtained intermittently. Several samples of CMS precursor resin were analysed, showing significant variation between batches (± 1.5%) and between beads (± 0.3%). Since the chlorine content of the precursor varies, so will the capacity of the product(s). This unfortunately limits the accuracy of conversion estimates by the

elemental analysis technique. Synthetic residue in precursors (commercial or otherwise) may have also introduced errors. This residue was not thoroughly extracted in every case, e.g. the bulk synthesis of CMS-2. As a result of these combined errors, calculation of the loading of benzo- and pseudo-crown ether resins confers considerable variability. Negligible differences between the GMA precursor and its pseudocrown derivatives do not permit their analysis in this way. The actual capacity of these materials would be best assessed by *in-situ* testing.

The derivation of capacity from elemental analysis data flows from the calculation of 100% conversion, as follows:

- The concentration of anchor groups per gram in the precursor resin was calculated (Q).
- The mass added and removed by conversion of all anchor groups into the desired moiety was calculated, per gram of precursor.
- The mass of a 100% yield of product from one gram of resin was calculated (Z).
- The mass of moiety added per gram was broken down into the abundances of specific elements, and these proportions were added to the elemental make-up of one gram of the precursor.
- In an analogous manner, proportional elemental mass equivalent to leaving groups was then subtracted from the precursor.
- The new elemental totals were then renormalised by dividing by Z.

Thus, the maximum capacity a resin may achieve is [Q/Z] milli-equivalents per gram. In practice, the yield was calculated from the proportion of each element compared to precursor and 100% yield figures. This can be found thus:

$$\% \text{ Yield} = \frac{100 \times (\text{Product} - \text{Precursor})}{(100\% \text{ Yield} - \text{Precursor})}$$

The Product, Precursor and 100% Yield figures are the abundances of a specific element in the relevant polymer. Three or four results could be obtained, but a reliable indicator should be any abundant element which changes significantly from precursor to product. The "Other" result should provide close confirmation; the substantially smaller H values vary too greatly for significant application. From the degree of conversion (% Yield), the resin capacities were calculated.

The following resins were analysed via this method: benzocrown- and pseudocrown-ether resins CMS-(9-16), GMA-(4-5) and GMB-1; hydrolysed epoxide GMA-2; aminocarboxylate resins DMA-1 and CMS-(5-8) and carboxylate resin MMA-3. It was recognised that these results contain a high degree of variability, and may be influenced by other factors such as side-reactions and substrate decomposition. The calculated capacities of CMS-pseudocrown products were poor to negligible. This is most likely a result of short reaction times, and poor kinetics in long-chain PEG syntheses. Small changes in the elemental content of the analogous GMA precursors and products also decreased the accuracy of

their calculated capacities. However, the C, H and O content of hydrolysed methacrylate MMA-3 was clearly consistent with ~75% hydrolysis.

The degree of conversion of amine resins to aminocarboxylates was also considered. This was conducted by calculating the increase in oxygen in a carboxymethylated resin from the amount and type of nitrogen present in the precursor, wherever possible. Other calculations apply as discussed previously. Difficulties were pronounced, as the actual analyses varied significantly from expected values. It can be concluded that resin CMS-5 was not carboxymethylated at every amine site, and a similar caveat applies to resins CMS-(6-8). The resin DMA-1 was anticipated to be fully carboxymethylated, but the elemental analysis of the sodium-form deviated from the expected pattern. This could not be readily explained by the presence of sodium or HCl adsorbed in the resin. Damage to the substrate may have occurred, or unexpected side-reactions.

2.2.2 Infra-Red Spectrometry

Fourier-transform diffuse reflectance Infra-red spectra were obtained from a single particle of bead material, and from fragments or a powder of copolymeric material. Copies of the FTIR spectra are included as Appendix I. Five materials were studied by IR, with comparison to the literature spectra of similar polymers and monomers where possible.

The urethane-type material PUR-1 showed a spectrum similar to a that of a copolymer of toluene 2,4-diisocyanate and ethylene glycol. Crosslinking via urea bond formation was also a common feature in the reference product [37]. The length of the poly(ethylene glycol) chain was the major difference. Strong peaks at ca. 1710, 1640, 1610 and 1540 cm^{-1} are indicative of several carbonyl environments, principally 2- and 4-urethane and urea groups. There is also evidence of abundant ethyl ether groups at 2960, 2940, 2850, 1450, and 1350 cm^{-1}, and the large peak at 1070 cm^{-1} is consistent with an ethyl urethane. Amide protons and adsorbed water appear in broad peaks at 3400-3300 cm^{-1}. Aromaticity is scarcely evident in the spectrum, probably enveloped in layers of polyether chain.

The radical polymerisation product CMA-2 shows the presence of methacrylic esters and ethers (2960, 2880, 1730, 1450, 1310, and 1250 cm^{-1}). The PEG-400 diacrylate chains should contain nine glycol subunits on average. The peak at 1120 cm^{-1} indicates that some residual unsaturated groups may remain. A broad peak at ca. 3400 cm^{-1} originates from water adsorbed into the relatively hydrophilic matrix.

Comparably, the substrate CMA-3 is prepared from PEG-600 and should bear fourteen glycol units per chain, on average. The sharply defined peaks of the transesterified product give more detail than CMA-2, with more pronounced alkyl peaks at 2980, 2950, 1200 and 1150 cm^{-1}. The spectrum compared very well with that of CMA-2 in most other respects,

other than a less pronounced peak at ca. 3400 cm^{-1}, and the absence of vinylic groups.

The peaks observed in the spectrum of MMA-4 were quite broad, but did not show substantial evidence of primary amine groups. Strong, broad OH/NH peaks at 3400-3300 cm^{-1} shadow a weaker peak at 3100 cm^{-1}. The two carbonyl stretching peaks observed at 1650 and 1570 cm^{-1} correspond to the methyl ester and amide, respectively. A strong peak at 1065 cm^{-1} may originate from OH or NH groups. Weaker absorbances at 2930, 2880, 1440, 1390, 1320, 1285, 1225, and 900 cm^{-1}, are consistent with aliphatic ester or amide structure.

The precursor resin GMA was also studied by FTIR, to establish the presence of epoxide groups. Carbon-oxygen stretching vibrations for the polymeric epoxide moieties were found at 1260, 910 and 850 cm^{-1} [38]. Other bands at 2950, 1730, 1455, 1390, 1150 cm^{-1} indicated the structural aliphatic ester groups. A broad peak centred at 3545 cm^{-1} may be due to some hydrolysed epoxide groups (2,3-dihydroxypropyl esters), or to adsorbed water on the surface.

2.2.3 Gravimetric Analysis

The *water content* of each sample was evaluated from the weight difference in a known mass of resin between wet and anhydrous states. Each resin sample was fully immersed in d.i. water, filtered, and then

surface water absorbed with dry filter paper [4]. This left only the water entrained within the pores, and hydrating the fixed ionogenic groups. The resin was then weighed, dried in a 60°C oven to constant mass (> 48 hours), and weighed again. The results have been reported as the percentage water in wet resin, and are included in Tables 2.1 - 2.5. The low temperature avoids side reactions which may contribute slightly to the loss of mass, such as decarboxylation or the formation of anhydrides. Products MMA-2 and GMA-8 were not evaluated in this manner, as no significant reference sample remained.

Resin volume changes upon adsorption or desorption of water were not generally measured. It is of note that the hydrated volume (and water content) of a fixed mass of resin can change dramatically between ionic forms. For example, the sodium salt form of resin MMA-3 swelled to several times the volume of the protonated resin, and five times that of the anhydrous resin. This effect was most dramatic in the high capacity weak-acid resins (MMA-2, MMA-3, and MMB-2), but applies to all ionogenic groups [4].

2.2.4 Microphotography

Optical and electron microscopy have been commonly employed for the study of the physical character of porous resin beads [3]. Only qualitative information about the integrity and swelling state of the resins can be obtained. Deformations or fractures can provide evidence of

osmotic shock and other structural damage. Preferably, a large number of beads are studied to assess the abundance of distorted or damaged beads. A series of microphotographs were obtained for the resins MMA-3, DMA, and DMA-1.

Optical microscopic analysis of resin MMA-3 revealed considerable physical damage to the substrate after hydrolysis. Fragments of shattered beads were abundant, and a fragile shell was observed around many of the beads, indicative of a severely hydrolysed outer layer. Much of this damage may have been introduced in the washing step subsequent to hydrolysis, due to rapid adsorption of water and resultant excessive swelling (osmotic shock). The three-fold difference in size between the water-swollen Na^+ and H^+ forms of MMA-3 is evidence of a very high capacity, and may also indicate decreased crosslinking.

Less destructive effects were observed on the commercial product DMA, an acrylic polyamine. Optical microscopy revealed that the DMA resin contained many spheres with a brittle shell less than 10 μm thick (Appendix II; Fig. (a) and (b)). This trait also appeared in the carboxymethylated product DMA-1 (Appendix II; Fig. (c)). The microspheres of both materials were substantively intact and undeformed, and were found suitable for bulk synthesis.

The MMA-1 microphotos reveal the problematic nature of anchoring a polyamine on a methacrylic substrate (Appendix II: Fig. (d)

and (e)). Amalgamated and distorted beads are evidence of either amide crosslinking, or softening and annealing of the substrate, or both. The proportion and nature of any tris(2-aminoethyl)amine crosslinking has not been investigated The highly functionalised methacrylic backbone is again very susceptible to osmotic shock (Appendix II: Fig (f)).

2.2.5 Titration of Fixed Ionogenic Groups

As a functionalised polymer bead bears a fixed number of ionogenic moieties, they may be titrated in a fashion similar to acid or base solutions. If all the ionogenic groups of a resin are forced into a common ionic form, they may be slowly titrated with a strong acid or base of known concentration. A known mass of a weak acid resin in protonated form can be titrated with strong base (NaOH). The titre of base correlates to the number of acidic groups available, thus the effective capacity of the resin (H^+ -> Na^+). Similarly, a weak base resin in free-base form can be titrated with strong acid (HCl). The mean pK_a of the ionogenic functional group appears at the mid-point of neutralisation. A number of such titrations were conducted on the resin products by other researchers [39]. Titration results for polyamine resin MMA-1, and copolymer CMA-1 in strand (a) and block (b) form, are shown in Table 2.8.

Whilst the most relevant form of analysis to the intended application of the materials, titrations were not comprehensively performed. All resin titration data used were obtained from other Geo2

consultants [39]. Time constraints limited the use of titrimetric analysis, which needed to be rigorously treated to derive useful results [4, 6]. Additional problems were encountered with aminocarboxylate moieties, which show complicated interaction between the acid and amine moieties. The titration of these moieties was not extensively investigated.

Resin Code	Functional Group	mean pK_a	DWC meq/g	% Water
MMA	methyl ester	n/a	< 0.01	19
MMA-2	carboxylic acid	3.65	0.35	59 (H^+)
MMA-3	carboxylic acid	3.09	0.45	59 (H^+)
MMB-2	carboxylic acid	3.73	0.13	69 (H^+)
MMA-1	tris(2-aminoethyl)amine	3.25	1.28	51 (H^+)
MMB-1	tris(2-aminoethyl)amine	2.48	0.34	72 (H^+)
MMC-1	tris(2-aminoethyl)amine	n/a	< 0.01	2.2 (H^+)
CMA-1 (a)	tris(2-aminoethyl)amine	3.82	0.075	73 (H^+)
CMA-1 (b)	tris(2-aminoethyl)amine	4.91	0.08	72 (H^+)
CMS-5	*sym*-DTTA	1.98	0.40	43 (H^+)
DMA-1	*asym*-DT3A	1.61	0.75	43 (H^+)

Table 2.8 Titration Results of Selected Resin Products

(Dry Resin Capacity meq/g, Water Content in H^+ form)

2.2.6 Metal Ion Adsorption Isotherms

The sorption of metal ions from solution by a sample of resin was used to derive characteristic resin isotherms [4]. After a common preconditioning, a series of resins was compared in terms of their capacity

to remove metal ions from batches of a common "head" liquor. Each resin was contacted with a fixed volume of head liquor for a given period of time, and the remaining metal ion concentration measured. The resins were then regenerated and the process repeated with a new head solution. A graph, or *Isotherm* can be derived from these data, comparing the concentration of ions within the resin to that of the external solution. In this way, the performance of resins under these conditions may be usefully compared.

In the present work, it was decided to assess the distribution of copper (II) ions between resin and solution in aqueous HCl at pH 2. The range of initial head liquor concentrations was between 10 - 150 ppm. The resins used were as follows: CMS-1, CMS-2, CMS-5, CMS-6, CMS-7, CMS-8, DMA, DMA-1, MMA-1, MMB-2, and GMA-1. This allows comparison between 1°-amine, carboxylate, and aminocarboxylate resins, anchored upon five varieties of substrate.

Each resin sample was preconditioned as follows:

A sample of resin was settled with de-ionised (d.i.) water in a 10 mL measuring cylinder, to a volume of between 6.0 - 6.2 mL. The resin was then placed in a tall, narrow liquid chromatography column and settled as d.i. water washed through the beads. The column was then washed through with a series of solutions (≥6 bed volumes each), each taking ≥15 minutes to pass through the resin. All resin washing steps below are of similar nature. The solutions were d.i. water, dil. aq. NaOH (0.010 M), aq.

NaOH (1.0 M), dil. aq. NaOH (0.010 M), d.i. water, dil. aq. HCl (0.010 M), aq. HCl (1.0 M), and finally dil. aq. HCl (0.010 M). The pH of the wash liquor was tested at each phase to ensure adequate washing. The last solution had pH = 2.0, the same as the copper(II) test solution. An electronic pH meter was used to ensure the pH was correct, although it should be noted that the accuracy of the instrument below pH 2.0 is increasingly unreliable. Each resin was filtered from this solution and dried by suction, then weighed (air-dry).

The copper isotherms were determined by the reduction of metal concentration in a 100 mL solution of $CuCl_2$ in 0.010 M HCl (pH = 2). After one hour of contact between a resin and a batch of the test solution, with occasional agitation, the liquor metal ion concentration was measured. An Atomic Absorption Spectrometer was used to determine copper content of the head, and the liquor above each resin in turn.

Regeneration of the resins (stripping) was achieved via elution with several bed volumes of strong aqueous acid (1.0 M HNO_3, then 1.0 M HCl). This was followed by washing with dil. aq. HCl (0.010 M) until the wash solution was pH = 2.0. The excess acid solution was then removed by suction on sintered glass, and the resin readied for re-use.

The results of these tests are given in the isotherms contained in Fig. 2.4 (Amine Resins) and 2.5. (Aminocarboxylate Resins). For both these groups of resins, time vs. copper adsorption graphs were also

produced for a 24 hour period (Fig. 2.6 and Fig. 2.7). It is notable that, in the absence of cyclic pumping or constant agitation, over 24 hours is required to attain equilibrium.

It was recognised that systematic errors were introduced through variations in several experimental parameters, as follows. In addition to measurement error in solution volume (± 0.05 mL), the volume of wash solution retained in the resin dilutes the head (± 0.50 mL). Significant variation was also encountered due to variations in the time at which measurements were taken (± 30 minutes). Evaporation of solvent may have also influenced solution concentrations over many hours, in competition with the precipitation of copper salts. Loss of resin capacity may result from chemical degradation, fouling, or bead attrition by osmotic shock. A few beads were also lost in transfer, and the AAS inlet required occasional unblocking from stray bead fragments and debris. Head concentrations were periodically measured and corrected to combat this effect. A net variation of ca. 10% (up to ± 50 ppm) is expected to apply to the metal concentration in the resin phase, i.e. the vertical scale in the isotherm graphs (Fig. 2.4 - 2.7).

2.2.7 Remediation Tests (*in-situ* Application)

Throughout the project, Geo2 Laboratories and the CSIRO Division of Minerals conducted tests to determine the efficacy of a resin in the intended application. A fixed mass of a standard soil contaminated with

heavy metal was leached in aqueous acid lixiviate, and the leach liquor was then contacted with the resin for a fixed time. Subsequent contact with strip liquor removed the metals, and the cycle was repeated. Criteria for a useful resin included negligible attrition of resin capacity, and bead integrity, over 1000 cycles. From this development, resins DMA-1 and CMS-2 were found suitable for pilot-plant testing.

The majority of the remediation testing results is contained within the combined Quarterly Reports for Action Gold/Geo2 Toxic Waste Remediation Project [39]. These results shall not be detailed or elaborated upon in this thesis due to their commercial sensitivity.

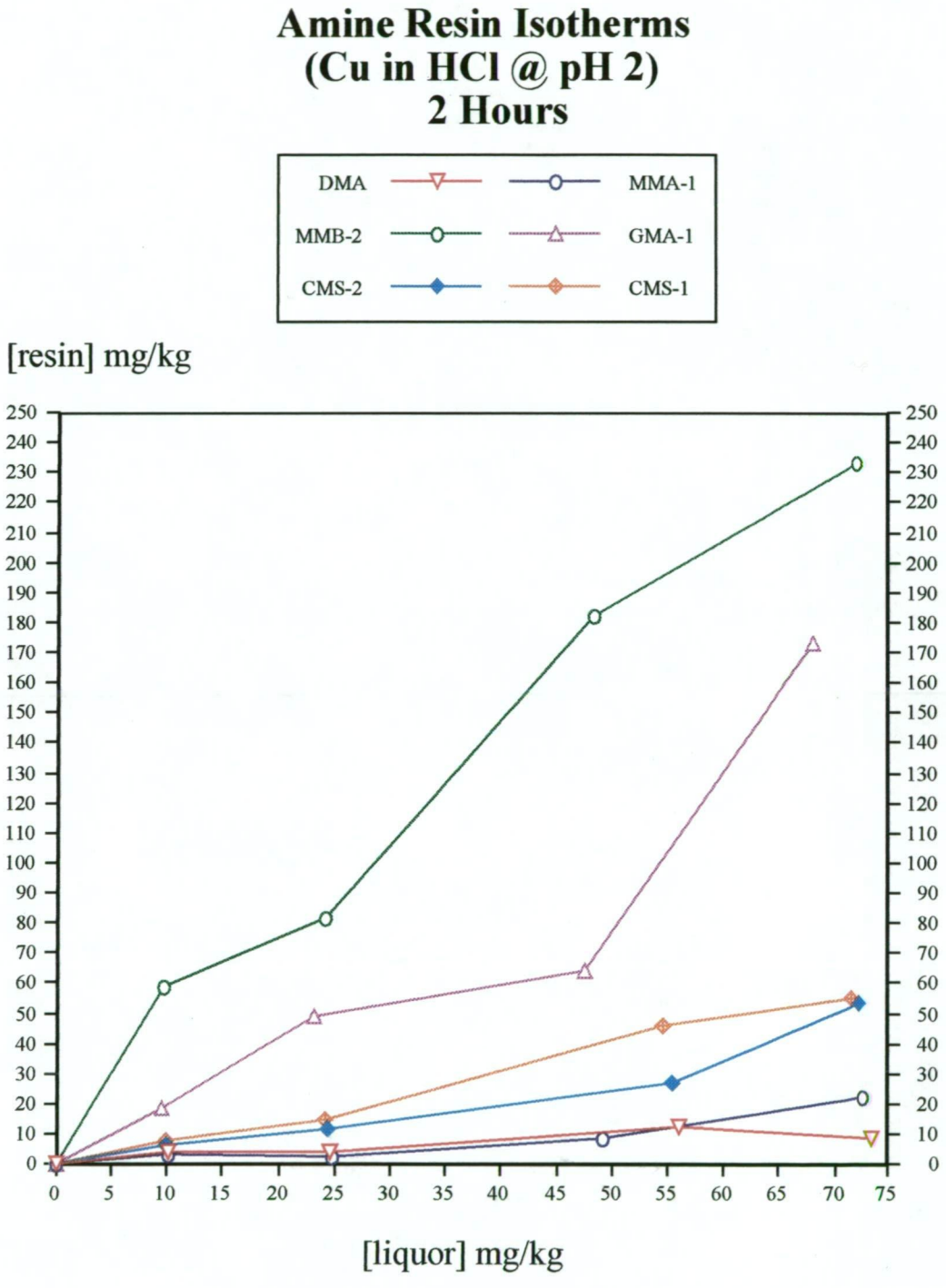


Figure 2.4 Amine Resin Copper(II) Isotherms

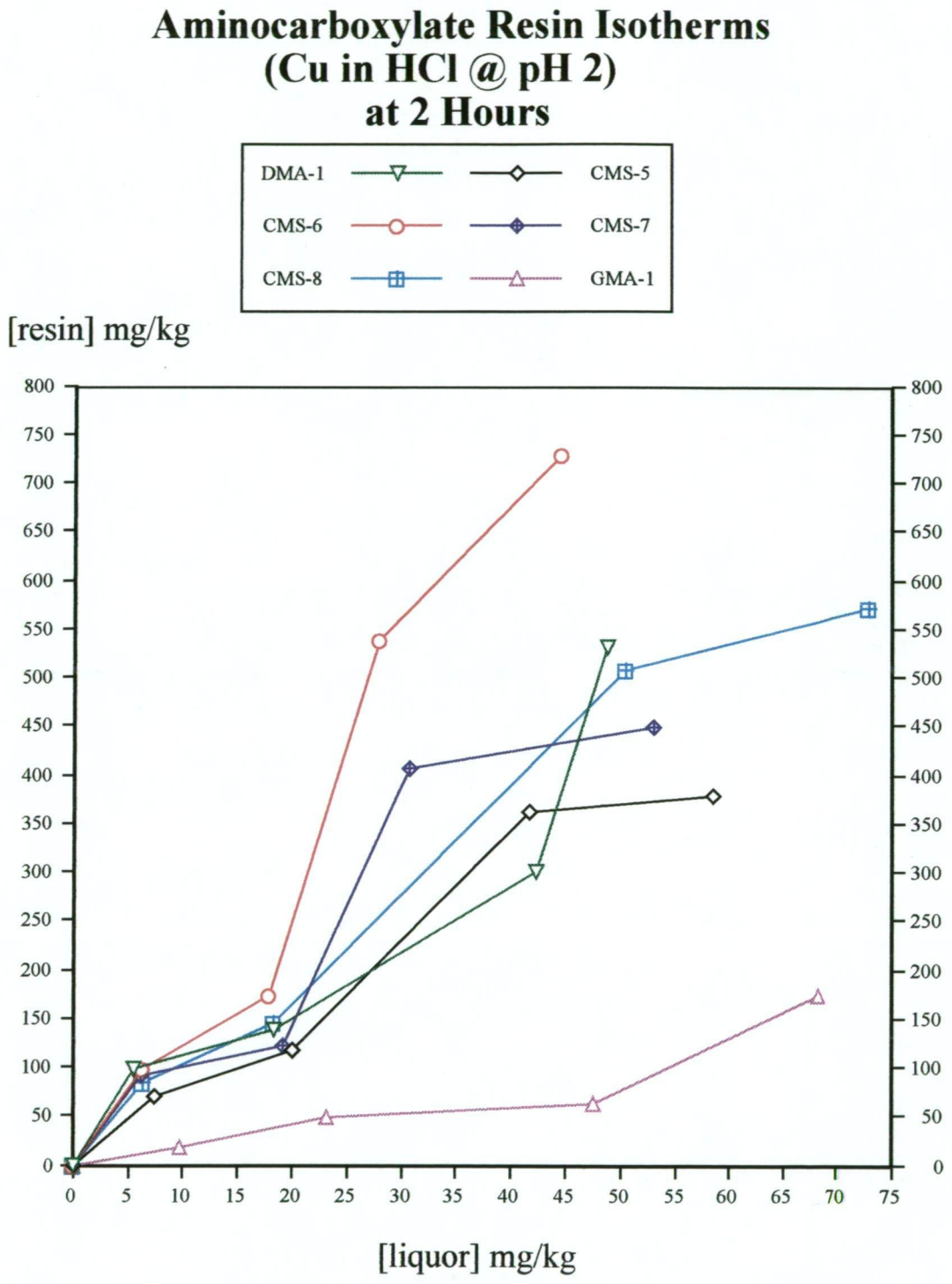


Figure 2.5 Aminocarboxylate Resin Copper(II) Isotherms

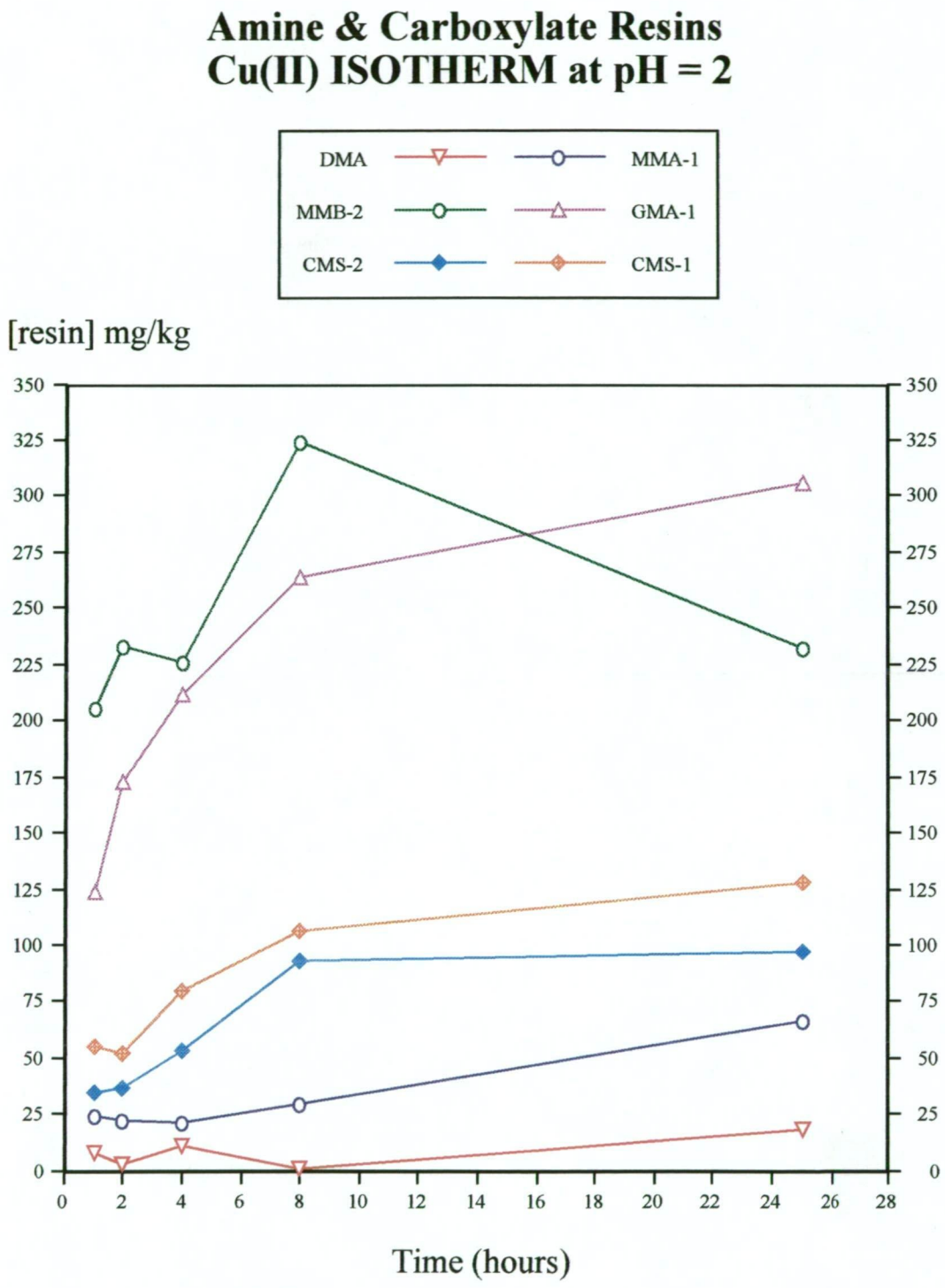


Figure 2.6 Amine Resin Copper(II) Absorption vs Time

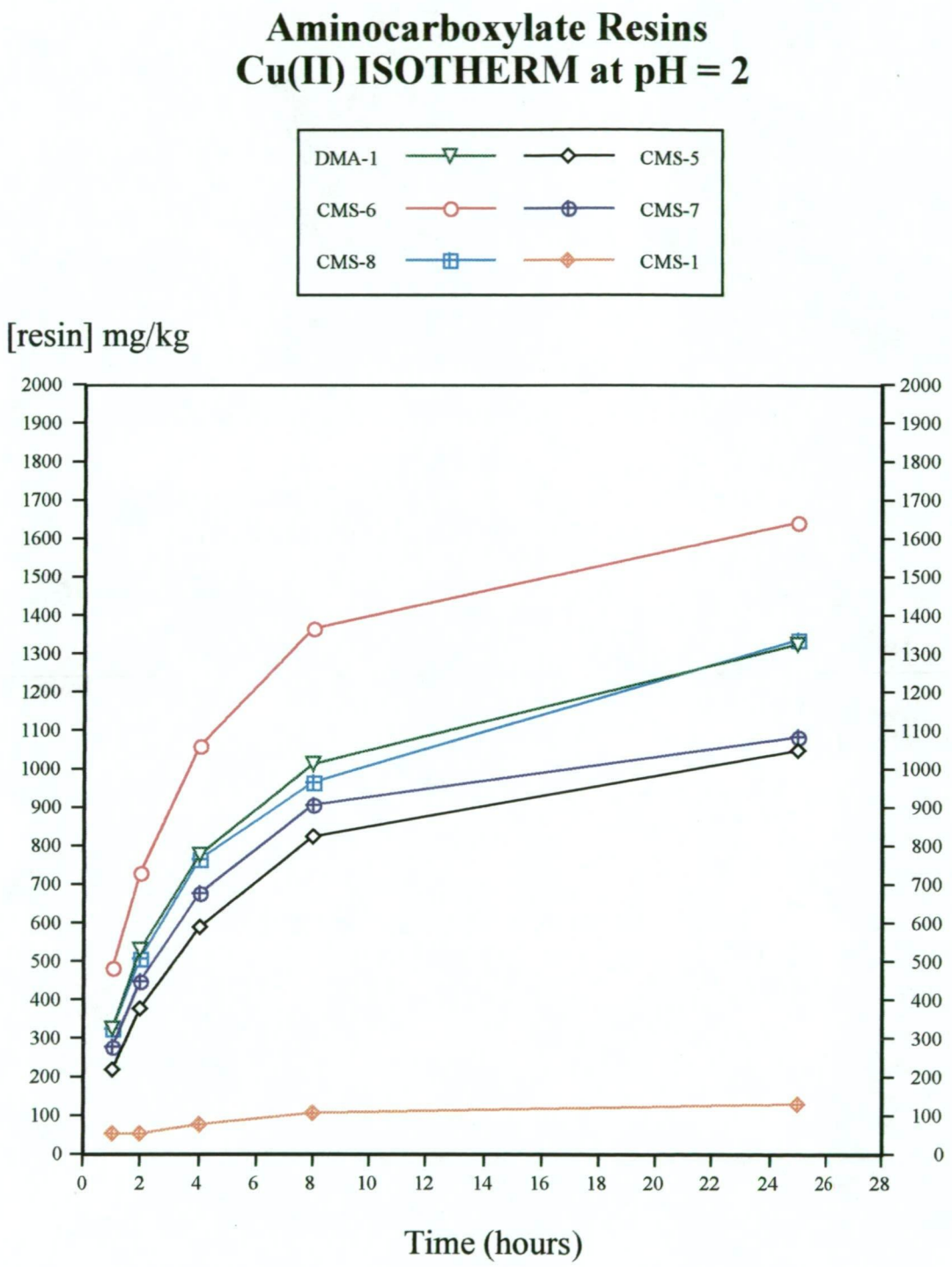


Figure 2.7 Aminocarboxylate Resin Copper(II) Absorption vs Time

3. CONCLUSIONS :

3.1 Resin Capacity and Metal Sorption

Although other characterisation information has been obtained, the utility of a chelating or ion-exchange resin is probably best assessed by a process simulating the remediation of a selected heavy metal. Copper is a common ion in contaminated areas, and is readily studied by spectroscopic methods. Thus, the isothermal distribution between copper(II) in the resin and in the supernatant solution was used. Independent assessment of several of the resins via the development of Cu(II) isotherms may be compared to the earlier characterisation results. These isotherms are somewhat crude, as in many cases the mass of resin used to determine the isotherm comprised the entire reference sample. The raw data are tabulated in Appendix IV (AAS & Isotherm Tables). Pseudocrowns and crown ether resins were not included in the development of the copper isotherms, as their activity was expected to be insignificant in standard aqueous conditions.

3.1.1 Isothermal Cu(II) Distribution

The isotherm data have been developed in two groups: a range of Cu^{2+} solutions in 0.01 M aqueous HCl were examined after 2 hours of resin contact; and a solution of Cu^{2+} (75 ppm) was equilibrated with the resins over 24 hours. It is important to note that, under the conditions used, equilibrium between the resin phase and the liquor was only established after $\geq$ 24 hours. This result is more evident with the aminocarboxylate resins (Fig. 2.7) than the amine resins (Fig. 2.6) which adsorbed little copper in any case. Resin CMS-1 is included in both figures

to facilitate easy comparison of the two groups. The protonation of amine ligands is likely to hinder the adsorption of the cationic $[Cu(H_2O)_6]^{2+}$ complex by coulombic repulsion. The α-hydroxyalkylamine GMA-1 and the carboxylate resin MMB-2 (Fig. 2.6) stand as intermediate examples, although the low mass of the latter has introduced significant error. Suppressed ionisation of the carboxylate resin, and the possible chelating character of GMA-1, may explain these anomalies.

The analogous isotherm for the aminocarboxylate resins (Fig. 2.7) demonstrated that each of the chelating resins behaved similarly. The greatest apparent capacity was found in the iminodiacetate resin CMS-6, more than 20% above that of the nearest rivals DMA-1 and CMS-8. The shapes of the adsorption curves were all substantively similar, indicating little difference in the resin kinetics. An important factor in the efficient sorption of metals into resins is the time taken to achieve equilibrium. Shorter equilibration times may be achieved by various forms of solution agitation, such as column pumping or countercurrent flow.

The distribution of Cu^{2+} ions between each resin and its supernatant was measured after 2 hours, using at least four different head liquor concentrations. These isotherms incorporate a more significant error margin than those measured at 75 ppm over time, and can be further complicated by processes such as the degradation of resin capacity. The maximal capacity of a resin may be implied by a change in the slope of such an isotherm, although none was expected in the range explored. The copper concentrations measured in the resin phase were invariably less than 2% of expected resin capacity.

Of the amine resins, only the resin GMA-1 showed significant adsorption. The isotherms of resins CMS-1 and CMS-2 lie within error margins of the equilibrium line, indicating that the Cu^{2+} ion was indifferent to the resin. Resins MMA-1 and DMA seem to have unfavourable isotherms under these conditions. The congruence of the behaviour of resins CMS-1 and CMS-2, and that of products MMA-1 and DMA, may be more indicative of the differences in substrate than functional group. The methacrylic amine resins appeared to be significantly less amenable to the adsorption of Cu^{2+} than similar GMA or CMS based resins. Water content did not appear to be a significant factor in this effect. It is expected that the 2-hydroxypropyl anchor group in each amine moiety of resin GMA-1 contributed significantly to copper adsorption in this resin. This was outperformed by carboxylate resin MMB-2; it is suspected that a precipitative effect may have applied.

The aminocarboxylate resin isotherms showed considerably more deviation from the expected smooth curves (Fig. 2.5). The most likely cause is the variation in time at which the readings were taken. In combination with the fact that equilibrium has not been established, this gives a resin phase error margin of ± 20%. On this basis, the iminodiacetate resin CMS-6 performed best, absorbing over sixteen times the liquor concentration. It is hard to distinguish the resins CMS-7, CMS-8 and DMA-1, whereas CMS-5 seemed to exhibit marginally poorer copper absorption. This agrees well with capacities derived from elemental analyses (Table 2.3, p.35). Again, it is suspected that the high capacity methacrylate polymer DMA-1 was less amenable to copper adsorption than the polystyrene matrices. The best performing amine resin GMA-1 is also included to facilitate comparison with Figure 2.4.

The most effective methacrylic resin for the adsorption of Cu(II) at pH 2 was certainly DMA-1, which was significantly less effective than the polystyrene based iminodiacetate resin CMS-6. The simple alkylamines showed little effect at pH 2, most likely due to abundant protonation of the resin. It was noted that the branched α-hydroxyalkylamine ligand of GMA-1 may have some utility at the operational pH. It should be noted that the resin behaviour observed was pH specific. Other supernatant solutions with similar copper concentrations may be used to derive isotherms at neutral or basic pH values. In conditions of high pH, the amine resins are expected to be significantly more effective in the adsorption of metal ions. Moreover, even minor changes (e.g. pH ± 0.5) would be expected to show significant changes in the behaviour of aminocarboxylate ligands.

3.1.2 Correlation with Resin Capacity

Reasonable correlation was found with the calculated capacity (from elemental analysis) and the relative absorption (from copper isotherms) of the aminocarboxylate resins. The isotherm data for the amine resins were consistent with calculated capacities, in terms of the number of amine groups per unit mass. This implied the presence of abundant protonated ammonium (chloride) groups in the resins. Similar abundances of amine groups are expected in both DMA and MMA-1, and likewise for CMS-1 and CMS-2. Titration results were less useful, with the action of the apparently very low-capacity carboxylate resin MMB-2 remaining unclear. The swelling behaviour of the carboxylate resins MMA-2 and MMA-3 was also inconsistent with the low titres reported.

The calculated capacity may err greatly if there are significant side-reactions such as crosslinking, as suspected in the case of MMC-1. The other two methacrylic tris(2-aminoethyl)amine resins (MMA-1 and MMB-1) have significant porosity as demonstrated by their water content. The lack of porosity in MMC-1 may be due to bis- and tris-amide crosslinking, or collapse of pores via annealing in synthesis. It has been reported that polystyrene resins have a glass transition temperature of 102-133°C, and similar temperatures apply for methacrylate resins [3]. In many of the products, some groups may also remain inaccessible to aqueous reagents, temporarily (as in MMA gel-type resins) or permanently (becoming entrained within backbone).

The capacities of the crown- and pseudocrown-ether polymers may be insignificant in many cases. Insufficiently vigorous reaction conditions may be responsible, such as the low reaction temperatures and times for CMS based materials. It is suspected that many chloromethylated sites were unavailable to alkylation by a long-chain PEG, as the bulky reagent makes reaction kinetics prohibitively difficult. Similarly, reactions between PEG and glycidyl methacrylate polymers lacked a strong acid or base to encourage attack at the epoxide. In both cases, the abundant PEG may have encouraged the formation of glycols anchored to the backbone by one end only. It is reported that polyalcohols give only solvation effects, with minimal ion-exchange effects [6].

The difficulty in ascertaining accurate capacity information also contributed to the problems with these polymers. Low to moderate capacity resins yielded elemental analyses significantly close to their precursors. Synthesis residues may have contributed to the inaccuracy inherent in the elemental analyses, to a degree that the determination of

their capacities was not reliable. Time constraints did not allow the complete characterisation of the products by more rigorous processes. The results of the crown- and pseudocrown-ether polymer syntheses therefore remain in doubt.

The principal problem with the determination of resin capacities from their elemental analyses was the large variations observed between beads. This variation was of similar size to the changes expected in the preparation of low to moderate capacity crown- and pseudocrown ether resins. This difficulty can only be minimised by comprehensive extraction of the entire batch of polymer, followed by pulverisation of a large quantity of resin beads in an inert atmosphere. The fresh powder should then be dried in the dark at or below room temperature over several days. This would prevent contamination of the elemental content by side-reactions, such as oxidation or the quaternization of amines, and by the adsorption of gases.

Comprehensive resin preconditioning should also occur prior to adsorption tests or titrations. After comprehensive extraction or reaction residues, resins should be cycled through the operational pH range several times. After ageing the wet resin for a few weeks, and washing a few times with an organic solvent and then water, the resins should be in suitably comparable states [6].

3.2 Commercial Resin Development

The lifetime and robustness of a functionalised resin are significant factors for an industrial process. It is often the case that the first few process cycles run with a fresh batch of resin show significant entrainment of metal ions or solids in the resin. The resin becomes 'attuned' to the process environment, and operates with smoother recoveries after this initial adsorption. This is consistent with the Donnan effect, in that multivalent ions are preferred over monovalent ions, which tend to reduce aqueous swelling [4, 6]. The dilution of external solution enhances the effect, and some ions may become permanently trapped within the resin. After this initial conditioning, the resin capacity should only gently decline with use over many cycles.

A useful characteristic to find in a resin is selectivity for a given metal ion. Selectivity for valence and hydrated ion size is known in some ion-exchangers, as well as ion-pair selectivity. Unfortunately, the utility of a resin in a multiple metal-ion solution cannot readily be ascertained without extensive testing. High background levels of common ions such as calcium, magnesium and iron can significantly complicate a chelating or ion-exchange equilibrium. The leach liquor is often modified by the addition of adjuvants to maximise the adsorption of heavy metals. If the process is then able to strip liquors to statutory environmental limits, then low-grade ores may also become commercially viable [40].

The bulk scale preparation of resins DMA-1 and CMS-2 demonstrates that the sorbents fulfil the requirements at least as far as pilot plant stage. Both resins have high capacities, and have shown to be robust in process conditions with little or no degradation of the resins

observed after 1000 cycles [39]. It is convenient that both resins are prepared via relatively simple techniques, as the scale-up of a more complicated resin would be prohibitively expensive. The relatively small groups introduced allowed the preparation of high capacity resins without prolonged reaction times or strict synthesis environments.

3.2.1 Concluding Remarks

The objectives of this project appear to have been met: a collection of 47 resins with chemically anchored carboxylate, alkylamine, and aminocarboxylate ligands was produced and compared. Doubt remains on the character and effectiveness of the macrocyclic ether sorbents, which presented considerably more difficulty in their syntheses and analyses. The preparation of bulk quantities of two of the products, CMA-2 and DMA-1, indicates that the development of useful sorbents has entertained significant success. Further investigation of the relationship between the structural properties of a polymer-bound ligand and heavy metal absorption may be conducted. Using the variety of amine, aminocarboxylate, and macrocyclic ether sorbents prepared, variations in both the substrate and the moiety may be studied in appropriate conditions, and useful features identified.

A number of approaches to the preparation of sorbents were scarcely touched in this work, and may be worthy of further investigation. It has been suggested that the binding of transition metals may also be effected using diazapseudocrown ethers (DAPOC) [31]. These ligands are much like the macrocyclic pseudocrown ethers, with the anchor groups being amines instead of ethers. High capacity sponge-like sorbents are

known which hold polyamine groups [41]; a DAPOC based porous sorbent may be a useful development. Metal selective sorbents have been prepared via alloying and/or copolymerisation [42-44]. In the current work, the preparation of substrates from monomeric or 'prepolymer' material was only investigated briefly, with a view to low-porosity or solid products. Such sorbents would be especially long lived if the slow attrition of the surface merely uncovers fresh layers of the adsorbing moiety. Although they have low surface area, the longevity and robustness of a solid in a rapid processing environment may win out in a commercial application. Nonetheless, the remarkable surface area of porous copolymer beads makes them the primary choice for the preconcentration and isolation of heavy metals.

4. EXPERIMENTAL :

4.1. Preliminary

Resin syntheses have been divided into three categories: porous polystyrene beads, porous methacrylic beads, and copolymer products. In some cases a synthesis was performed several times, usually denoted as *(a)*, *(b)*, *(c)*, and so on. Reactions utilising resin beads were mechanically stirred via a teflon blade on a glass rod entering through a Liebig condenser. Reactions between GMA or GMB resins and poly(ethylene glycol)s were stirred via a stainless steel paddle and rod. An atmosphere of dry nitrogen was provided for all syntheses not performed in aqueous media. Unless specified otherwise, all resins were dehydrated by heating to 65°C in a vacuum oven at ≤ 5 mm Hg for at least 12 hours prior to elemental analysis or IR spectra.

Petroleum ether (light alkanes, b.p. 60-80°C) was dried by standing over calcium chloride. Absolute ethanol was obtained via distillation from over calcium hydride under nitrogen. Benzene was distilled from over sodium wire under nitrogen, whereas 1,4-dioxane was distilled from over sodium hydride or sodium wire under nitrogen. Toluene was redistilled and dried by standing over calcium hydride. Anhydrous chloroform was obtained by distillation from over active P_2O_5. Catechol was recrystallised from neat benzene and dried on a vacuum line. Sodium hydride in non-volatile alkane oil (60% NaH w/w) was used. Where specified, anhydrous poly(ethylene glycol) (PEG) was prepared by heating the reagent to 100°C under vacuum (<1.0 mm Hg) for 2 hours, agitated via stirring or with a tiny nitrogen "bleed". De-ionised water was

used throughout. Other commercial reagents were used without further purification unless specified otherwise.

Infra-red spectra were obtained using a Bruker IFS-66 FTIR spectrometer. Elemental Analyses were provided with a Carlo Erba EA1108 instrument, and reported as percentages of carbon (C), hydrogen (H) and nitrogen (N) where appropriate. Copper(II) isotherm concentrations were measured with a Varian SpectrAA-800 Atomic Absorption Spectrometer (AAS), which was calibrated using five standards at pH 2. Atoms were generated in an oxidising acetylene/air flame, and measured at an emission wavelength of 217.9 nm (at a current of 4 mA and slit width 0.2 nm). Three measurements from each sample were combined to obtain the mean copper concentration. Gas chromatography/mass spectrometry was performed with a HP-5890 GC coupled to a HP-5970B mass selective detector, using a 1 μL splitless injection to a HP-1 column (He/15 psi). Injection temperature was 260°C and oven temperature was 60 - 290°C, increasing at 10°C per minute. Scan range was M/Z = 14 - 400, at 1 scan per second. Liquid Secondary Ion Mass Spectra (LSIMS) were obtained via a Kratos Concept ISQ LSIMS source and probe, driven by a 10 KV primary beam of Cs^+ ions accelerated by 5.3 KV. The scan range was M/Z = 100 - 2000, at a rate of 2 seconds/decade and a resolution of 1000. Nuclear Magnetic Resonance (NMR) spectra were obtained for a number of precursor reagents using a Varian Gemini-200 NMR spectrometer. Carbon spectra were obtained at 50 MHz, and hydrogen spectra at 200 MHz, with results reported in ppm. Proton peak multiplicity was denoted by (s) singlet, (d) doublet, (t) triplet, (m) multiplet, and (b) broad peak, with proton coupling constants reported as J_H. Carbon peaks were reported as (s) strong, (m) medium, and (w) weak. TMS (tetramethylsilane) at 0.00 ppm was used as an internal standard.

4.2 Precursors

The following section encompasses two analyses of precursor substrates not included in Table 2.7, and the preparation of several reagents which were used in resin syntheses. Elemental analysis was conducted on CMS and DMA beads, dehydrated in a vacuum oven at 65°C for 18 hours @ 5 mm Hg (Table 4.1).

Polymer	Carbon	Hydrogen	Nitrogen	Other
CMS (i)	71.66	6.33	-	22.01
CMS (ii)	72.57	6.36	-	21.07
DMA	60.36	9.54	22.48	7.62
DMA (wet)	30.32	5.31	10.82	53.55

Table 4.1 Elemental Analyses of Precursor Resins

Chloromethylated macroporous polystyrene (CMS) was extracted with methanol, and dried for 18 hours at 65°C @ 5 mm Hg. Elemental analyses of two whole resin beads are compared above, reported as CMS (i) and (ii). Significant variation was observed in the analyses of samples that had not been extracted. Nonetheless, the bulk synthesis of CMS-2 was conducted without prior extraction of synthesis residue. The analysis of a fully hydrated sample of DMA in free-base form was also performed. The water of hydration encompasses the "Other" category, corresponding to a capacity of 2.58 meq/g (wet).

4.2.1 Reagent Syntheses

(i) Protection of Diethylenetriamine with Salicylaldehyde

Neat diethylenetriamine (10.06 g, 97.5 mmol) was added to a solution of salicylaldehyde (23.74 g, 194.4 mmol) in absolute ethanol (100 mL) at ambient temperature. The reaction mixture became warm and yellow, and was stirred without further heating for 30 minutes. Removal of the solvent via rotary evaporation left a quantitative yield of bis(salicylidineimino)diethylenetriamine [abbreviated Dien(Sal)$_2$]. The product was a yellow oil which still contained residual ethanol. Slow evaporation over several days allowed this material to solidify, producing long needle-like bright yellow crystals.

bis(salicylidineimino)diethylenetriamine

^{1}H-NMR (200 MHz, DMSO-d_6) : δ= 1.22 (t, J_H = 7.0 Hz, 1H); 2.99 (b.t, J_H = 5.6 Hz, 2H); 3.70 (t, J_H = 7.0 Hz, 3H); 6.81 - 6.94 (m, 2H); 7.19 - 7.33 (m, 2H); 8.34 (s, 1H). ^{13}C-NMR (200 MHz, DMSO-d_6) : δ = 18.41 (m); 49.66 (m); 58.15 (w); 59.42 (m); 116.96 (s); 118.61 (s); 131.35 (s); 132.28 (s); 161.07 (m); 166.16 (m)

(ii) Synthesis of DCPEG-400 in Toluene

PEG-400 (200.368 g, 500.9 mmol) was combined with toluene (500 mL) and pyridine (87.429 g, 1.105 mol) in a 1.0 L flask topped with a condenser. The flask was cooled in an ice-bath and flushed with dry nitrogen, and thionyl chloride (119.147 g, 1.001 mmol) was added dropwise. The mixture became a warm white suspension, slowly yellowing. The mixture was left to stir overnight under a $CaCl_2$ tube. The orange mixture with white ppt. was heated to 80°C with vigorous stirring, becoming an opaque orange suspension. After 1 hour, the reaction was cooled and water (100 mL) was slowly added to quench excess $SOCl_2$. This was stirred for 30 minutes, then the phases were separated and the

aqueous phase back-extracted with ether (3 x 50 mL). The combined organic layers were extracted with aq. HCl (0.25 M, 250 mL), then stirred for 10 minutes with saturated aq. $NaHCO_3$ (200 mL). The organic phase was washed again with water (3 x 250 mL) and dried over Na_2SO_4 for a weekend. Filtering off the drying agent and rotary evaporation of the residue yielded 92.783 g of yellow oil, corresponding to a ca. 42.5% yield of α,ω-dichloro(poly(ethylene glycol)) [DCPEG-400].

Conventional GC/MS (Gas Chromatography/Mass Spectra) analysis could only be performed on the lighter fractions (e.g. PEG-200). The larger polyglycols are not volatile enough for gas chromatography. LSIMS relies upon commercial PEG fractions as internal standards, and is thus readily applied to the current synthetic products. Determination of constituent ratios has been elucidated from the peak heights of the products. LSIM spectra of five commercial PEG fractions (PEG-200, 400, 600, 900, 1000) have been obtained for use as references (Appendix III: (ii) - (vi)). Major fragmentation ions were consistently observed at m/z = 133.1 and 177.1, as well as dehydroxylated species (M^+ - OH). Also note that fragmentation of the larger glycols has increased the abundance of the shorter polymers. A LSIM spectrum of the DCPEG-400 product was obtained (Appendix III: (vii)).

(iii) Preparation of DCPEG-600 in Benzene

PEG-600 (199.988 g, ca. 333 mmol, dried at 100°C in vacuo) was dissolved in anhydrous benzene (500 mL, distilled from over sodium wire) and pyridine (58.960 g, 745 mmol, distilled from over sodium wire). The mixture was mechanically stirred while cooling in an ice bath, and thionyl chloride (83.401 g, 701 mmol) was added dropwise as dry nitrogen was passed through the vessel. After some initial fuming, the mixture

became cloudy white. Upon complete addition of $SOCl_2$ (45 minutes), the white slurry was stirred for another 30 minutes and then heated in a boiling water-bath to a gentle reflux. This was maintained for 30 minutes, then left to stand over the weekend under dry nitrogen. Water (250 mL) was cautiously added to the orange solution (containing white ppt.) and stirred for 30 minutes. The aqueous phase was isolated and back-extracted with diethyl ether (3 x 70 mL); the combined organic phases were then washed with water (150 mL) and aqueous HCl (0.25 M, 225 mL). The solution was then stirred for 30 minutes with aqueous $NaHCO_3$ (1%, 2 x 250 mL) with copious evolution of gas. The organic mixture was washed further with water (6 x 150 mL) and the organic phase dried over Na_2SO_4 overnight. The solids were then filtered off and the solvent removed on a rotary evaporator to leave 13.639 g of yellow oil [DCPEG-600] (ca. 6.4%).

(iv) Preparation of DCPEG-600 in Toluene

A batch of PEG-600 was dried by stirring at 100°C on a vacuum line (ca. 1 mm Hg) for two hours. Pyridine was distilled from over KOH in a nitrogen atmosphere. PEG-600 (200.312 g, ca. 334 mmol) and pyridine (56.080, 709 mmol) were dissolved in redistilled toluene (400 mL), and fitted with a condenser and a dry nitrogen inlet. Thionyl chloride (84.080 g, 707 mmol) was added dropwise while the reaction vessel was cooled in an ice-bath. The resulting white mixture gave off white fumes, and was left to stir overnight at room temperature under an atmosphere of dry nitrogen. The mixture was then heated to 80°C in a water bath for 1 hour, then cooled and quenched by cautiously adding water (100 mL). The resulting bilayer was shaken with water (250 mL) and the aqueous layer separated and back extracted with ether (3 x 50 mL). The combined organic phase was then extracted with aqueous HCl (0.25 M, 250 mL) and stirred with aq. $NaHCO_3$ (1%, 250 mL), causing evolution of much gas and froth.

The aqueous bicarbonate layer was then removed, and the pH determined to be basic (pH 8). The organic phase was the washed further with water (3 x 250 mL) and dried over Na_2SO_4. After filtering off the drying agent, the solution was rotary-evaporated to leave 16.257 g of yellow oil [DCPEG-600] (ca. 7.7% yield).

Seven sets of PEG related peaks were observed in the gas chromatogram of the first batch of DCPEG-600, in the expected semi-gaussian distribution (Appendix III: (viii) - (x)). Each set of peaks consists of a triad comprising poly(ethylene glycol) (PEG), its monochlorinated isomer (MCPEG), and the dichloro product (DCPEG). The starting PEG is the least abundant (ca. 5%), with the monochlorinated product in greatest abundance (ca. 80%) and the dichloro product comprising the remainder. Deviation from this pattern is observed in the last triads, in which the DCPEG is in greatest abundance. Products were identified from mass spectra of the fourth triad by the presence or absence of the following M/S peaks : PEG {m/z = 45 (C_2H_5O), 75 ($C_3H_7O_2$), 89 ($C_4H_9O_2$)}; DCPEG {m/z = 63 (C_2H_4Cl), 93 (C_3H_6ClO), 107 (C_4H_8ClO)}. The second synthesis of DCPEG-600 appears to have been more effective (Appendix III: (xi) - (xii)).

The decreasing yield of DCPEG-600 appears to indicate that shorter PEG precursors were more susceptible to the reaction. Syntheses of longer DCPEG products gave negligible yields. The presence of monochlorinated by-products in the reagents unfortunately limits the efficacy of subsequent syntheses. Further purification of DCPEG products was deemed impractical, and no method was found to enhance the yield.

4.3 Polystyrene Resins

4.3.1 Amines on Polystyrene

(i) CMS-1 : tris(2-aminoethyl)amine

A batch of CMS (60 mL) was combined with tris(2-aminoethyl)amine (ca. 200 mL, excess) and slowly heated to 80°C with gentle stirring under dry nitrogen. After 4 hours, the mixture was cooled and filtered, and the resin washed with methanol (2 x 200 mL), de-ionised water (5 x 200 mL), aq. HCl (1%, 3 x 300 mL), and finally more water (3 x 200 mL). The resin was forced into free-base form by washing with excess aq. ammonia (5M), then dried in vacuo. Elemental analysis yielded 75.39% C, 7.60% N and 8.01% H.

(ii) CMS-2 : *p*-aminomethylated polystyrene

(a) A sample of anhydrous CMS beads (ca. 108 g, 220 mL) was combined with sodium iodide (0.346 g, 2.31 mmol), hexamethylene tetramine (111.105 g, 792.5 mmol) and methanol (300 mL). The mixture was shaken thoroughly and left to stand overnight, then stirred gently via glass/teflon stirrer for 24 hours at room temperature. The beads were filtered off and washed with methanol (2 x 250 mL), water (2 x 250mL) and again with methanol (250 mL). The swollen white beads (ca. 350 mL) were combined with conc. aq. HCl (175 mL) in methanol (350 mL) and refluxed for 2 hours. After filtering, the beads were washed with water (2 x 300 mL), and left to stand in a mixture of conc. NH_4OH (100 mL) and water (200 mL) for 5 hours. The polymer was filtered off and washed with water (2 x 250 mL), and the stored wet. Elemental analysis of dry CMS-2 yielded 79.88% C, 7.82% H, and 6.82% N.

(b) A sample of CMS resin (250 mL) was washed with water (500 mL), then methanol (300 mL), and washed into a 1.0 L flask with more methanol (750 mL). This mixture was shaken thoroughly with sodium iodide (0.153 g, 1.02 mmol) and hexamethylenetetramine (125.1 g, 892 mmol), and left to stand for 4 days with occasional shaking. The polymer swelled to ca. 400 mL during this time. The polymer was then filtered off and washed with methanol (2 x 300 mL), then with d.i. water (5 x 250 mL). Afterward, the beads were suspended in a mixture of methanol (450 mL) and conc. aq. HCl (225 mL), and the mixture refluxed for 2 hours. The green-hued mixture was cooled, filtered, and washed with d.i. water (2 x 250 mL), and left to stand for three days in aqueous ammonia (~5M, 500 mL). Finally, the polymer was washed with d.i. water (4 x 1000 mL).

(c) A batch of CMS (250 mL) was washed with methanol (350 mL) and added to a solution of hexamine (100.0 g, 713.3 mmol) in methanol (600 mL). The stoppered mixture was shaken thoroughly, and occasionally shaken over the next 7 days at room temperature. The polymer was filtered on a glass frit with suction, and washed with methanol (2 x 300 mL) to leave ca. 450 mL of swollen yellow beads. These beads were suspended in a mixture of methanol (500 mL) and conc. aqueous HCl (250 mL), and refluxed for 2.5 hours. The mixture was filtered and washed with methanol (200 mL), then water (5 x 300 mL). This material was stored wet in ammonium chloride form.

(d) Bulk-scale apparatus (20 L capacity) was constructed for the synthesis of 200 litres of CMS-2 resin (Appendix V). The synthesis was conducted using five litre batches of resin, without prior extraction of residues from the CMS precursor. CMS was stirred for two days with excess hexamine, then washed with methanol and refluxed for two hours

in methanol and hydrochloric acid. After washing, small quantities of the resin product from three random batches were put into hydrochloride form, then dried in a vacuum oven. Samples from two other batches were put into free-base form. The results of these elemental analyses are incorporated into Table 4.2.

% C	% H	% N	% Other	Form	DWC (meq/g)
63.77	7.72	5.10	23.41	$-NH_3Cl$	3.64
70.24	7.88	5.20	16.68	$-NH_3Cl$	3.71
70.20	8.17	5.55	16.08	$-NH_3Cl$	3.96
76.20	8.06	5.63	10.11	$-NH_2$	4.02
69.28	7.72	4.92	18.08	$-NH_2$	3.51

Table 4.2 Elemental Analysis of CMS-2 from Bulk Synthesis

(iii) **CMS-3** : ethylamine

A sample of CMS-2 resin (110 mL) was left to stand for 4 hours in aqueous ammonia solution (5M, 2 x 250 mL) and rinsed with de-ionised water (4 x 250 mL), then acetone (2 x 200 mL). The resin was suspended in dry acetone (250 mL) and ethyl iodide (23.169 g, 0.149 mol). This mixture was refluxed for 18 hours, cooled and filtered, and the resin washed with acetone (200 mL), methanol (200 mL), aqueous $NaHCO_3$ (10%, 200 mL), aq. HCl (0.1 M, 250 mL) and finally d.i. water (4 x 200 mL). The volume of the magenta product was approximately 120 mL. Elemental analysis of the dry free-base resin yielded 74.45% C, 8.04% H, and 5.63% N.

(iv) **CMS-4** : isopropylamine

A vacuum-dry sample of CMS-2 (60 mL) in free-base form was suspended in chloroform (250 mL), and isopropyl iodide (24.967 g, 147 mmol) was added. The mixture was heated to reflux for 14 hours. The

polymer was filtered off and washed with methanol (2 x 300 mL), then water (2 x 200 mL). The polymer was left to stand in dilute aqueous NaOH solution (ca. 1%, 2 x 400 mL) for 30 minutes. Finally, the beads were washed with d.i. water (4 x 350 mL). The anhydrous free-base resin comprised 82.67% C, 6.48% N, and 8.53% H.

(v) **CMS-20** : triethylamine

A sample of CMS resin (110 mL) was suspended in methanol (175 mL) and triethylamine (45.0 mL, 0.323 mol), was added dropwise. The suspension was then refluxed for 18 hours, cooled and filtered, and the resin was washed with methanol (2 x 200 mL), water (250 mL), aqueous HCl (1%, 250 mL), and finally more water (3 x 250 mL). The volume of the wet product resin was approximately 140 mL. A small batch of the resin (ca. 5 mL) was washed with excess aq. sodium carbonate (1 %), then water, and dried in a vacuum oven. Elemental analysis showed 74.52% C, 9.64% H and 3.43% N

(vi) **CMS-21** : diethylamine

CMS resin (110 mL) was suspended in methanol (175 mL) and diethylamine (33.0 mL, 0.319 mol) was added dropwise. The mixture was then refluxed for 18 hours, and the red suspension cooled and filtered. The resin was washed with methanol (2 x 200 mL), water (250 mL), aqueous HCl (1%, 250 mL), and water (3 x 250 mL). The volume of the wet product was approximately 130 mL. A small batch of the resin (ca. 5 mL) was washed with excess aq. sodium carbonate (1 %), then water, and dried in a vacuum oven. Elemental analysis of they dry resin gave 78.96% C, 8.75% H and 3.98% N.

(vii) **CMS-22** : diethanolamine

A batch of CMS resin (110 mL) suspended in methanol (200 mL) was combined with a solution of diethanolamine (34.650 g, 0.330 mol) in methanol (50 mL). A catalytic quantity of sodium iodide (ca. 100 mg) was added and the suspension was then refluxed for 20 hours. The mixture cooled and filtered, and the resin was washed with methanol (250 mL), then water (4 x 250 mL) leaving approximately 120 mL of wet resin. A sample of the resin (ca. 5 mL) was washed with excess aq. sodium carbonate (1 %), then water, and dried in a vacuum oven. Elemental analysis of they dry resin gave 73.78% C, 7.92% H and 3.45% N.

(viii) **CMS-23** : *n*-octylamine

To a 500 mL flask containing CMS resin (60 mL, 500-900 μm) was added *n*-octylamine (30.007 g, 232.2 mmol), followed by sodium iodide (ca. 200 mg) and methanol (250 mL). The mixture heated to reflux for 24 hours under dry nitrogen gas, then cooled and filtered. The beads were washed with methanol (100 mL), water (500 mL), dilute aq. HCl (1%, 2 x 400 mL) and finally more water (3 x 400 mL). A sample (ca. 5 mL) was washed with excess aq. ammonia (1 M) and dried in vacuo. Elemental analysis of the product gave 81.49% C, 8.89% H, and 2.80% N.

(ix) **CMS-24** : benzylamine

A sample of PS-009 (60 mL, 500-900 μm) was combined with benzylamine (30.122 g, 281.1 mmol), sodium iodide (ca. 200 mg) and methanol (250 mL). The yellow mixture was refluxed for 22 hours under dry nitrogen gas, and then cooled and filtered. The beads were washed with methanol (100 mL), water (500 mL), dilute aq. HCl (1%, 2 x 400 mL) and finally more water (3 x 400 mL). A small sample (ca. 5 mL) was

washed with excess aqueous ammonia (1 M) and dried in vacuo. Elemental analysis resulted in 83.81% C, 7.70% H, and 3.60% N.

(x) **CMS-25** : ethanolamine

A sample of CMS beads (60 mL, 500-900 μm) in a 500 mL flask was combined with ethanolamine (23.101 g, 378.2 mmol), followed by sodium iodide (ca. 200 mg) and methanol (250 mL). The mixture was stirred under dry nitrogen gas and heated to reflux for 18 hours, then cooled and filtered. The beads were washed with methanol (150 mL), dilute aq. HCl (1%, 2 x 350 mL) and water (3 x 500 mL). After washing a ca. 5 mL sample of the resin with excess aqueous ammonia (1 M) and drying in vacuo, elemental analysis yielded 79.12% C, 8.07% H, and 3.82% N.

(xi) **CMS-26** : *t*-butylamine

To a 500 mL flask containing sample of CMS resin (60 mL, 500-900 μm) was added *t*-butylamine (23.350 g, 319.3 mmol), followed by sodium iodide (ca. 200 mg) and methanol (300 mL). The mixture was stirred and heated to reflux for 18 hours under dry nitrogen gas, cooled and filtered. The beads were washed with methanol (100 mL), dilute aq. HCl (1%, 2 x 400 mL) and water (3 x 500 mL). A small sample (ca. 5 mL) was washed with excess aq. ammonia (1 M) and dried in a vacuum oven. Elemental analysis of this sample gave 80.25% C, 8.52% H, and 3.12% N.

(xii) **CMS-27** : isopropylamine

A sample of CMS resin (60 mL, 500-900 μm) was combined with isopropylamine (22.146 g, 375 mmol), sodium iodide (ca. 200 mg) and methanol (300 mL), and heated to 45°C (±5°C) for 20 hours under dry nitrogen gas. The mixture was then cooled and filtered, and the beads were washed with methanol (150 mL), dilute aq. HCl (1%, 2 x 350 mL) and

water (3 x 400 mL). A small sample (ca. 10 mL) was washed with excess aqueous ammonia (1 M) and dried in vacuo. Elemental analysis of this sample of resin gave 80.54% C, 8.41% H, and 3.59% N.

4.3.2 Aminocarboxlates on Polystyrene

(i) CMS-5 : *sym*-DTTA (diethylenetriamine tetraacetic acid)

(a) A sample of CMS beads (200 mL) was washed with ethanol (200 mL) and dried overnight at 80°C. This was added to a solution of Dien(Sal)$_2$ (50.01 g, 160.6 mmol) in dry dioxane (400 mL) and refluxed under a $CaCl_2$ tube for 18 hours. The resulting grey-brown suspension was filtered and washed with ether (400 mL), leaving brown beads in a yellowish precipitate. This was washed with water (3 x 300 mL), and the beads were washed into aqueous HCl (6 M, ~250 mL) and stirred at 60°C for 24 hours. The brown resin beads were isolated by filtration, and washed with water (3 x 250 mL), ethanol (2 x 200 mL) and then stirred in aqueous NaOH (2 M, 200 mL) for 2 hours. The beads were filtered off again, washed with water (6 x 150 mL) and ethanol (2 x 150 mL), and added to a solution of sodium chloroacetate (100.3 g, 860.8 mmol) and sodium carbonate (18.67 g, 176.2 mmol) in water (800 mL). This mixture was stirred at 55-70°C for 30 hours, then cooled and filtered. The resin was washed with water (200 mL), aqueous HCl (2 M, 2 x 200 mL), water (3 x 300 mL), ethanol (200 mL) and ether (200 mL). Elemental analysis yielded 72.62% C, 6.77% H and 2.48% N.

(b) A sample of CMS (200 mL) was washed with water (200 mL) and dried at 80°C for 24 hours. The beads were then swelled in stirred dioxane (250 mL) for 1 hour and combined with Dien(Sal)$_2$ (100 g, 322 mmol) in dioxane (100 mL) and refluxed under a $CaCl_2$ tube for 48 hours. The

resulting tan slurry was filtered, washed with ether (200 mL), ethanol (2 x 250 mL) and water (2 x 250 mL). The yellow beads were then stirred in aqueous HCl (6 M, ~250 mL) at 50°C overnight, then 6 hours at 60°C. The brown resin beads were filtered off and washed with water (2 x 500 mL) and then stirred in aqueous NaOH (2 M, 350 mL) for 2 hours. The beads were filtered off again, washed with water (2 x 250 mL), and added to the residual sodium chloroacetate/sodium carbonate solution from *(i)*. This mixture was stirred at 70°C overnight, during which time most of the water evaporated. Water (500 mL) was added to redissolve the white precipitate on the beads, and the mixture stirred for a further 30 minutes, then filtered. Finally, the resin was washed with water (2 x 250 mL), stirred in aqueous HCl (5 %, 500 mL), and again washed with water (2 x 250 mL).

Elemental analysis of batch (ii) yielded 69.61% C, 3.69% H and 3.69% N. (This corresponds to a capacity of 0.87 meq/g of symmetric diethylenetriamine tetra-acetic acid groups (in HCl form, pH = 1), although the hydrogen analysis is ~ 2.5 % lower than expected).

(ii) **CMS-6** : Iminodiacetic acid

A sample of CMS-2 (110 mL, 500 - 850 μm) was rinsed with water (3 x 250 mL) and added to a flask containing sodium carbonate (30.843 g, 291.0 mmol), sodium chloroacetate (67.752 g, 581.7 mmol) and water (500 mL). The mixture was stirred until the solids dissolved, and then heated to 65°C for 18 hours (overnight). The reaction was cooled, and the orange-tan resin was recovered by filtration and washed with water (3 x 250 mL). Elemental analysis yielded 68.14% C, 7.19% H and 4.65% N.

(iii) CMS-7 : *asym*-DTTA (diethylenetriamine tetraacetic acid)

A sample of CMS (110 mL, 500-900 μm) was washed with methanol (2 x 250 mL), and placed in a flask fitted with an overhead stirrer, heating mantle and condenser. To this mixture was added fresh diethylenetriamine (77.569 g, 751.9 mmol), washed in with more methanol (250 mL). The mixture was gently stirred and refluxed overnight, cooling after 18 hours. The resin was filtered off, washed with methanol (2 x 250 mL) and water (3 x 250 mL). The polymer was transferred to a flask containing sodium chloroacetate (91.636 g, 786.7 mmol), sodium carbonate (41.710 g, 393.5 mmol) and water (350 mL). This mixture was stirred and heated to 65°C for 20 hours, then cooled and filtered. The pale yellow resin was washed with water (3 x 250 mL), and elemental analysis gave 76.74% C, 7.87%H and 6.71% N.

(iv) CMS-8 : *asym*-DTTA (diethylenetriamine tetraacetic acid)

A sample of large bead CMS resin was dried overnight at 80°C (110 mL), then swollen in 1,4-dioxane (300 mL). Freshly distilled diethylenetriamine (60.277 g, 584.2 mmol) was added, washed in with more dioxane (50 mL), and the whole mixture was refluxed under dry nitrogen for 18 hours. Upon cooling, the mixture was filtered and washed with dioxane (200 mL), then water (3 x 250 mL). The yellow beads were washed into a flask bearing sodium chloroacetate (67.405 g, 578.7 mmol), sodium carbonate (30.635 g, 289.0 mmol) and water (350 mL). This was heated to 65°C and left to stir for 18 hours, then cooled and filtered again. The yellow beads were washed with water (4 x 250 mL), and vacuum dried. Elemental analysis of this material gave 73.52% C, 8.03% H and 8.20% N. Note that the nitrogen content is greater than in CMS-7, most likely influenced by a favourable solvent (dioxane vs. methanol).

4.3.3 Crown- and Pseudocrown Ethers on Polystyrene

(i) CMS-9 : catechol (1,2-benzenediol)

(a) CMS beads (210 mL) were swollen in a solution of catechol (49.691 g, 451 mmol, recrystallised) in dry chloroform (600 mL). The reaction vessel was flushed with a stream of dry nitrogen, and stirred for 30 minutes. Subsequently, $SnCl_4$ (20 mL, ca. 171 mmol) was slowly injected over 10 minutes. The reaction mixture became a deep magenta colour, and a few white fumes of HCl were observed; after 30 minutes the mixture was deep red and white fumes could be seen at the top of the condenser. The reaction was gently heated to reflux on a heating mantle and maintained for 7.5 hours, then cooled and quenched by pouring the mixture slowly into 1.0 L of ice/water slurry, with stirring. The polymer was then filtered off and washed with water (300 mL), methanol (2 x 250 mL), conc. aq. HCl (250 mL), water (3 x 300 mL) and methanol (2 x 250 mL). The vivid purple beads were further washed with triethylamine (25 mL) in chloroform (225 mL), then neat chloroform (250 mL). Elemental analysis of the anhydrous resin yielded 76.36% C, 6.58% H, and 0.41% N. The presence of nitrogen may be attributed to synthesis residues, or to the conversion of some remaining chloromethylated sites into triethylammonium groups.

(b) A sample of dry CMS resin (360 mL) was swollen in anhydrous chloroform (500 mL) for 30 minutes. Some residue from within the beads gave a yellow colour to the solvent. A solution of catechol (95.358 g, 866.0 mmol, A.R. >99%) in warm anhydrous chloroform (300 mL) was added to the above mixture. The mixture was stirred under dry nitrogen and heated to reflux, whereupon some of the solvent (ca. 100 mL) was distilled off. The mixture was cooled to room temperature and $SnCl_4$ (40.0 mL, 342

mmol) was injected. The reaction became exceedingly vigorous, and HCl gas was observed leaving the top of the condenser. The mixture rapidly became deep purple, and was left to reflux for 20 hours. The milky purple suspension which resulted was cooled and filtered, producing HCl vapour and much white precipitate. The solids were washed with water (1.0 L), causing fumes of HCl to appear and allowing the white solids to dissolve. The resin was then washed with aq. HCl (6 M, 500 mL) and then water (4 x 500 mL), leaving a collection of magenta beads.

(ii) **CMS-10** : PEG-400 benzocrown ether

Into a 1.0 L flask containing NaH (60% in alkanes, 20.326 g, 508.2 mmol) was added CMS-9 (batch *(a)*, 160 mL) swollen in dry dioxane (700 mL). The mixture was stirred gently under nitrogen for 30 minutes as some gas was evolved, then DCPEG-400 (61.843 g, 141.6 mmol) was added dropwise over 1 hour, and washed in with more dioxane (50 mL). The mixture was then heated to 50°C and stirred for one hour, then cooled. When quenched with methanol (50 mL), much gas was evolved and a tan froth was generated. The mixture was left to stand for two days, filtered on a Büchner funnel, and washed with methanol (2 x 250 mL) and then water (6 x 250 mL). The resulting grey/brown polymer beads were dried in vacuo and subjected to elemental analysis, yielding 76.12% C, 6.63% H, and 0.20% N.

(iii) **CMS-11** : PEG-600 benzocrown ether

A sample of CMS-9 (b) catechol-polystyrene (60 mL) was stirred in 1-butanol (350 mL) for 30 minutes to allow full swelling. Subsequently, conc. aq. NaOH (10.0 mL) was added and stirred in for 1 hour. To this black solution was added the combined DCPEG-600 products (35.332 g, ca, 55.5 mmol). The reaction mixture heated slowly to 80°C (± 5°C) with

stirring. After 16 hours at this temperature, the mixture was cooled and filtered, and washed with 1 -butanol (100 mL), methanol (2 x 100 mL) and water (2 x 100 mL). The black beads were then stirred in a mixture of d.i. water (300 mL) and conc. aq. HCl (50 mL), becoming a tan colour. These beads were further washed with water (2 x 250 mL), and a sample (ca. 10 mL) was dried for elemental analysis. This showed a composition of 77.72% C, 7.09% H, and no nitrogen.

(iv) **CMS-12** : PEG-2000 pseudocrown ether

Anhydrous dioxane (250 mL) was added to a dry flask containing sodium hydride (60%, 11.463 g, 286.6 mmol) and CMS resin (~120 mL) under a blanket of dry nitrogen. This mixture was stirred for 30 minutes to permit full swelling of the resin, and then fragments of PEG-2000 (100.346 g, ca. 50.2 mmol) were slowly added over 10 minutes. Some gas was gradually evolved as the mixture was stirred for a further 2 hours at room temperature, and then at reflux for a further hour. The mixture was allowed to cool overnight, and was quenched by the addition of methanol (50 mL) over 30 minutes, with copious frothing. The mixture was filtered and the yellowish beads washed with methanol (3 x 200 mL), hot water (~85°C, 4 x 200 mL) and lukewarm water (3 x 200 mL). Elemental analysis showed the presence of 73.75% C and 7.22% H.

(v) **CMS-13** : PEG-1500 pseudocrown ether

A suspension of anhydrous CMS (125 mL) and sodium hydride (60%, 12.995 g, 324.9 mmol) in anhydrous dioxane (400 mL) under dry nitrogen was stirred for 30 minutes at room temperature. Molten PEG-1500 (109.378 g, 72.9 mmol) was added over 45 minutes, causing the voluminous formation of froth. The mixture was stirred at 20°C until no more gas was evolved, and then heated to reflux for 2 hours. After

allowing the reaction to cool, it was quenched by cautiously adding methanol (60 mL) and stirring for 30 minutes. The mixture was filtered and washed with water (~90°C, 2 x 250 mL, then ~20°C, 2 x 200 mL). Elemental analysis of the product yielded 75.14% C and 7.74% H.

(vi) **CMS-14** : PEG-900 pseudocrown ether

Under an atmosphere of dry nitrogen, an anhydrous solution of PEG-900 (52.0 g, 58 mmol) in 1,4-dioxane (~250 mL) was prepared, and sodium metal (2.634 g, 115 mmol) was added in tiny chunks. This mixture was stirred for 16 hours, and refluxed under a condenser for 5 hours. Waxy white solids were observed on the walls of the flask. A batch of anhydrous CMS resin (110 mL) was then added and stirred for 30 minutes, then the mixture was gently refluxed for 1 hour. The reaction was then cooled, and quenched by adding methanol (50 mL). This mixture was suction filtered over a glass frit and the polymer washed with methanol (250 mL), then water (4 x 350 mL). An elemental analysis of this polymer yielded 72.29% C and 6.58% H.

(vii) **CMS-15** : PEG-600 pseudocrown ether

To a solution of anhydrous PEG-600 (50.596 g, 84.33 mmol) in dry dioxane (300 mL) under dry nitrogen was added anhydrous CMS resin (110 mL). This was stirred for 15 minutes to allow for swelling, then sodium hydride (60%, 8.353 g, 209 mmol) was added over several minutes. A large volume of gas was evolved as the solution warmed and became frothy, and droplets of solvent began to collect in the condenser.

After 20 minutes of gentle stirring, the mixture refluxed for 1 hour as the solution slowly turned a light brown. The mixture was left to cool overnight under a blanket of dry nitrogen. The mixture was filtered and

washed with ethanol (300 mL), then water (4 x 350 mL). Elemental analysis of the product revealed 72.24% C and 7.28% H.

(viii) CMS-16 : PEG-600 pseudocrown ether

Anhydrous CMS (110 mL) was stirred and swollen for 1 hour in a solution of anhydrous PEG-600 (26.076 g, 43.46 mmol) in dry toluene (350 mL) under a blanket of dry nitrogen. Subsequently, dibenzo-18-crown-6 (250 mg, 0.69 mmol) was added in fresh toluene (20 mL). This was followed by sodium hydride (60%, 4.107 g, 103 mmol) suspended in four portions (each in 20 mL toluene), having been washed free of oil with of pet. ether (2 x 30 mL). Much gas was evolved, rapidly at first and then slowly over 30 minutes. The mixture was heated to 80°C and held at this temperature for 120 minutes, then cooled and quenched by adding methanol (50 mL) and stirring for 15 minutes. The polymer was filtered off and washed with denatured ethanol (250 mL), redistilled ethanol (200 mL), and water (4 x 300 mL). Elemental analysis of the resin gave 72.12% C and 6.41% H.

4.3.4 Control Sample Polystryene Resins

(i) CMS-17 : NaH quench in methanol

Anhydrous CMS beads (110 mL) were swollen in undistilled methanol (350 mL) for 30 minutes. Residue from within the beads caused the solvent to develop a yellow colouration. The mixture was stirred as sodium hydride (60%, 11.247 g, 281.18 mmol) was added in small portions over 10 minutes, under a blanket of dry nitrogen gas. A great deal of gas was evolved, and the exothermic reaction raised the temperature of the mixture to ca. 45°C. This was left to stir for 5 hours, and then quenched by pouring the whole reaction mixture into water (350 mL). The polymer

was filtered off and washed with methanol (2 x 200 mL), acetone (2 x 200 mL), and water (3 x 250 mL).

(ii) CMS-18 : sodium methoxide in dioxane

A sample of CMS resin (110 mL) was swollen in stirring anhydrous 1,4-dioxane (250 mL) for 30 minutes, and then dibenzo-18-crown-6 (253 mg, 0.70 mmol) was added. Meanwhile, small pieces of sodium metal (7.398 g, 322 mmol) were washed with petroleum ether and then suspended in anhydrous dioxane (100 mL) under a blanket of nitrogen gas. Over 90 minutes, crude methanol (60 mL) was added via a pressure-equalising dropping funnel until the sodium had completely dissolved. This mixture was then added to the suspension of swollen polymer, which was then stirred overnight. The mixture was quenched by the addition of saturated ammonium chloride solution (20 mL) and then vacuum-filtered. The polymer washed with denatured ethanol (250 mL), then water (3 x 300 mL).

(iii) CMS-19 : hydrolysis with methanol/HCl

A sample of CMS resin (60 mL) was combined with methanol (200 mL) and conc. aq. HCl (100 mL), and the resulting mixture refluxed (at 77°C ± 2°C) for two hours. After cooling overnight, the beads were filtered off and washed with water (4 x 150 mL). Elemental analysis of the product gave 71.21% C, 6.20% H, and no nitrogen.

4.4 Methacrylic Resins

4.4.1 Hydrolysis of Methacrylic Resins

(i) MMA-2 : poly(methacrylic acid)

A sample of MMA resin (100 mL) was combined with a solution of NaOH (100 g, 2.5 mol) in water (120 mL) and trimethylbenzylammonium chloride (22.617 g, 121.8 mmol). This was heated and stirred at 100°C for 2.5 hours, and filtered to leave ca. 500 mL of white polymer beads. These were stirred in aq. HCl (5%, 500 mL) at 50°C for 2 hours, washed with water (5 x 500 mL), and oven-dried at 100°C overnight.

(ii) MMA-3 : poly(methacrylic acid)

(a) A batch of MMA resin (200 mL) was suspended in saturated aq. NaOH (400 mL) and refluxed at ca. 110°C (± 5°C) for 2 hours. The caustic was filtered off, and the resin was washed with water (500 mL), causing the beads to swell rapidly (to ca. 900 mL). The hydrolysed resin was stirred in aq. HCl (5%, 500 mL) for 3 hours, maintaining pH ≤ 1 with litmus and aliquots of conc. HCl (20 mL). Filtration left 700 mL of transparent resin beads, which were oven-dried at 120°C to leave ca. 350 mL of hard white resin beads.

(b) Methacrylate beads (MMA, 75 mL) were refluxed in freshly prepared saturated aq. NaOH (300 mL) at 120°C (± 5°C) for 3 hours. The resin was then filtered off, washed with water (3 x 500 mL), and left to stand in ca. 300 mL of water. The pH of this solution was lowered by addition of conc. aq. HCl in 10 mL aliquots, testing pH periodically. When at pH = 7, the remaining 150 mL of beads were filtered off.

(c) Another batch of MMA beads (200 mL) was saponified in saturated aq. NaOH (1.00L) at 115°C (± 5°C) for 4 hours. The beads were isolated by filtration, and washed with water (1.0 L) until the pH of the supernatant solution was 7.00 (± 0.10). The pinkish sample beads were washed with water (300 mL), a sample was taken for titration, and the remainder of the sample (ca. 400 mL) was oven dried at 80°C overnight. A small batch of this resin (ca. 10 mL) was washed with excess aq. HCl (1%); elemental analysis of the anhydrous product gave 49.55% C and 6.14% H.

(iii) **MMB-2** : poly(methacrylic acid)

(a) A sample of MMB resin (60 mL) was stirred and heated to 120°C (± 5°C) in a concentrated solution of NaOH (300 mL) for 3 hours. The resin was then isolated by suction filtration, and washed with excess water. The swollen resin (ca. 400 mL) was dried in an oven at 80°C for two days, and the resulting white polymer was stored in a desiccator. A sample of this batch was subsequently analysed via titration.

(b) A sample of MMB resin (150 mL) was heated to 110°C (± 5°C) in concentrated aqueous NaOH with vigorous stirring for 90 minutes. The white beads were filtered off and washed with water (3 x 500 mL). The resulting swollen beads were then stirred in water as concentrated aqueous HCl was added dropwise until the pH remained acidic (<5) over 10 minutes stirring. The beads were then washed again with water (3 x 300 mL, leaving ca. 600 mL of translucent white microspheres.

(iv) **GMA-2** : 2,3-dihydroxypropyl poly(methacrylate)

A sample of GMA resin (<300 μm, 15 mL) was refluxed in concentrated aqueous HCl (100 mL) for 30 minutes. After cooling, the resulting greyish white resin (30 mL) was filtered off and washed with

water (3 x 100 mL). Elemental analysis of the dry product yielded 50.66% C and 6.32% H.

4.4.2 Aminolysis of Methacrylic Resins

(i) **MMA-1** : tris(2-aminoethyl)amine poly(methacrylamide)

(a) A batch of MMA beads (150 mL) was swollen in tris(2-aminoethyl)amine (110.335 g, 754 mmol) as the equipment was flushed with a steady stream of dry nitrogen. When slowly heated to 160°C (± 5°C) in a sand bath with vigorous stirring, reflux commenced. A clear fluid was collected in a distillation reservoir attached to a side-arm condenser. After a total of eight hours at 160°C, the resin was then filtered off. Extraction of the resin with ethanol in Soxhlet apparatus for 24 hours yielded 72.753 g (66%) of recovered tris(2-aminoethyl)amine. The product was further washed with water (3 x 300 mL). Elemental analysis of the dry resin yielded 52.02% C, 8.78% H, and 16.59% N.

(b) A sample of MMA resin (110 mL, >550 μm) was placed in a flask containing a teflon-coated magnetic stir bar. Under an atmosphere of dry nitrogen, tris(2-aminoethyl)amine (~100 mL) was added and the reaction vessel placed in a sand bath. The mixture was stirred into a slurry, and left stirring as it was slowly heated to 160°C under a condenser topped with a $CaCl_2$ tube. Over 3 hours, the beads expanded to absorb the majority of the reagent. The swollen aminolysed beads were cooled and extracted with methanol in Soxhlet apparatus for 24 hours. The yellow beads were then stirred in water (300 mL) for 2 hours before suction-filtering and rinsing with more water (300 mL).

(ii) **MMB-1** : tris(2-aminoethyl)amine poly(methacrylamide)

A sample of MMB resin (110 mL) was immersed in tris(2-aminoethyl)amine (150 mL). This mixture was stirred vigorously and heated to 160°C for one hour, causing the resin to expand to absorb the majority of the reagent. The mixture was cooled, and more tris(2-aminoethyl)amine (100 mL) was added. This was stirred and heated to 160°C again for 3 hours, as the solids had expanded to >250 mL. The excess tris(2-aminoethyl)amine was recovered from the solid polymer beads by suction filtration. The remaining swollen yellow beads were washed with ethanol (2 x 300 mL) and methanol (3 x 300 mL), stirred in water (300 mL) for 24 hours, and washed again with water (2 x 300 mL).

(iii) **MMC-1** : tris(2-aminoethyl)amine poly(methacrylamide)

A sample of MMC resin (100 mL) was stirred into tris(2-aminoethyl)amine (150 mL), which totally immersed the solid beads. As this mixture was stirred and heated to 130°C, the resin expanded to absorb the reagent. The mixture was cooled, and tris(2-aminoethyl)amine (50 mL) was added to suspend the solids. This was stirred and heated to 145°C for two hours, then to 160°C for one hour. The resin expanded >250 mL, and the vessel was cooled and the solid polymer filtered off. This was washed with methanol (3 x 500 mL), stirred in water (600 mL) for 8 hours, then filtered and washed with another 300 mL of water.

(iv) **GMA-1** : tris(2-aminoethyl)amine on glycidyl methacrylate

A sample of GMA resin (60 mL) was swollen in tris(2-aminoethyl)amine (150 mL) for 30 minutes under dry nitrogen. The mixture was then heated to 60°C and stirred vigorously for 16 hours. After cooling, the resin was filtered off and washed with water (3 x 300 mL), hydrochloric acid (5%, 2 x 250 mL), water (2 x 250 mL), and left to stand in

aqueous ammonia (5 M, 500 mL) for three hours. The product washed again with water (2 x 500 mL) and a sample was dried in a vacuum oven yielded 55.87% C, 8.54% H, and 8.85% N to elemental analysis.

(v) GMA-3 : 3-amino-2-hydroxypropyl poly(methacrylate)

A sample of GMA resin (60 mL) was cooled to -34°C in a stainless steel autoclave fitted with a pressure gauge and thermocouple, and anhydrous liquid ammonia (ca. 10 mL) was added (from a cylinder). The autoclave was sealed and heated (over 3 hours) to an internal temperature 80° C, reaching an internal pressure of 10 Bar. The vessel was discharged, cooled to ca. - 50° C, and more ammonia was added (ca. 20 mL). The autoclave was sealed again and slowly heated to 80°C (over 4 hours), at which temperature the pressure became 30.5 Bar. The vessel was left at this temperature for 2 hours, then allowed to cool overnight. The gas was released after 16 hours and the vessel left to return to room temperature (having cooled to ca. -20°C by evaporation). The white resin was left to stand for several hours to allow the ammonia to evaporate.

(vi) MMA-4 : ethanolamine poly(methacrylic ester/amide)

A sample of MMA beads (60 mL) was suspended in ethanolamine (250 mL). This mixture was heated under a dry nitrogen atmosphere until reflux commenced. A side-arm condenser was connected to remove volatiles, which appeared in the range of 110-165°C (ca. 20 mL collected). After four hours at 165°C (± 5°C) the apparatus was allowed to cool, and filtered to recover ethanolamine. The resulting swollen translucent white beads (ca. 150 mL) were washed with methanol (2 x 300 mL) and water (5 x 400 mL). Elemental analysis of the product yielded 52.26% C, 8.63% H, and 12.01% N.

4.4.3 Carboxymethylation of Methacrylic Resins

(i) **DMA-1** : DT3A (diethylenetriamine triacetic acid)

(a) A sample of DMA resin (200 mL) was added to a solution of sodium chloroacetate (116.695 g, 1.002 mmol) and sodium carbonate (54.214 g, 511 mmol) in water (600 mL). This mixture was heated to 60°C with vigorous stirring for 10 hours, and left to cool over a weekend. The resulting yellow/orange beads were filtered off and washed with water (5 x 500 mL). A small batch (ca. 10 mL) was washed with excess aq. HCl (1%) and vacuum dried. Elemental analysis resulted in 47.72% C, 7.51% H and 13.84% N.

(b) A solution of chloroacetic acid (164.0 g, 1.735 mol) in water (300 mL) was cautiously neutralised by slow addition of sodium carbonate (184.0 g, 1.736 mol). This solution was made up to 800 mL, and combined with the remaining 300 mL of DMA resin. The resulting mixture was stirred and heated to 70°C for a total of 12 hours, then the solids were filtered off and washed with water (3 x 500 mL). The beads were then stirred in HCl solution (ca. 3M, 600 mL) for 1 hour, filtered and washed with water (2 x 250 mL).

(c) Bulk-scale apparatus (20 L capacity) was assembled for the synthesis of 30 litres of DMA-1 resin. The reaction vessel was a polyethylene bucket, with a stainless steel immersion heater and a polyethylene paddle turned by an overhead stirrer. The vessel was drained via a low stopcock with an internal filter of fine polymer mesh (<100 μm). The synthesis was conducted using five litre batches of DMA resin, without any prior extraction of residues.

In a typical synthesis, DMA resin (5.0 L) was added to a solution of sodium carbonate (480.0 g, 4.53 mol) and sodium chloroacetate (2222.0 g, 19.08 mol) in 15 litres of de-ionised water. This mixture was vigorously stirred and heated to 65°C (± 5°C) for a total of twelve hours, then the aqueous liquor was drained off and the polymer was washed with water (3 x 8 L).

4.4.3 Methacrylic Pseudocrown Ether Resins

(i) **GMA-4** : PEG-900 pseudocrown ether

Molten PEG-900 (ca. 50°C, 180 mL) was added to GMA resin (110 mL, >300 μm) and slowly heated to 180°C under dry nitrogen with vigorous stirring for 2 hours. The resin was filtered off on a warm Büchner funnel, and washed with warm methanol (50°C, 250 mL), lukewarm methanol (250 mL), and then stirred in boiling water (200 mL) for an hour. The beads were filtered off again, washed with d.i. water (500 mL), and a vacuum dry sample yielded 57.19% C and 7.31% H upon elemental analysis.

(ii) **GMA-5** : PEG-200 pseudocrown ether

To a sample of GMA resin (60 mL) was added PEG-200 (150 mL). This was stirred and heated to 100°C for 3 days. The light tan mixture was filtered, and the polymer washed with methanol (2 x 100 mL) and hot water (85°C, 3 x 200 mL). Elemental analysis of the product gave 55.40% C and 7.66% H.

(iii) **GMA-6** : PEG-900 pseudocrown ether

GMA resin beads (65 mL, >300 μm) were combined with molten PEG-900 (ca. 50°C, 100 mL) and stirred vigorously with a stainless steel

shaft at 125°C for 20 hours. The mixture was then cooled to 50°C and filtered over a Buchner funnel, and washed with hot methanol (ca. 50°C, 200 mL), hot water (ca. 80°C, 200 mL), and then cold water (2 x 150 mL). The yellow polymer was then added to a warm solution of freshly pulverised KOH (12.821 g, 228.5 mmol) in absolute ethanol (200 mL). This mixture was stirred for several hours at room temperature, then heated to 80°C and stirred for a further hour. The mixture was then cooled, filtered, and washed with d.i. water (5 x 200 mL). Elemental analysis of the dry product gave 55.51% C and 7.72% H. This synthesis also produced some small yellow rubbery fragments which differed radically in appearance to the polymer beads.

(iv) **GMA-7** : PEG-2000 pseudocrown ether

Liquefied PEG-2000 (75°C, 120 mL) was combined with GMA resin (65 mL, >300 μm) and stirred at 115°C overnight. The mixture was filtered after 18 hours, and the yellowish beads were washed with hot water (85°C, 4 x 300 mL), then cold d.i. water (2 x 200 mL).

(v) **GMB-1** : PEG-900 pseudocrown ether

A sample of GMB resin (110 mL) was combined with molten anhydrous PEG-900 (65°C, 150 mL). The mixture was stirred and heated to 110°C for a total of 10 hours, then filtered in a Büchner flask at 80°C. The beads were washed with warm methanol (40°C, 2 x 100 mL), water (2 x 100 mL), hot water (60°C, 5 x 100 mL) and finally cold water (2 x 100 mL). Elemental analysis of the product gave 57.06% C, 7.52% H, and a negligible 0.10% N.

(vi) **GMB-2** : PEG-400 pseudocrown ether

A batch of GMB resin (60 mL) was immersed in PEG-400 and stirred under dry nitrogen at 110°C for 14 hours. The polymer was then filtered off, washed with methanol (2 x 100 mL) and water (4 x 100 mL, then 3 x 300 mL).

(vii) **GMB-3** : PEG-600 pseudocrown ether

A sample of anhydrous PEG-600 (250 mL) was combined with GMB resin beads (60 mL) and heated to 110°C under dry nitrogen gas with gentle mechanical stirring for 14 hours. The mixture was then filtered, and the beads were washed with methanol (2 x 100 mL) and water (4 x 200 mL). The volume of the white resin product was ca. 90 mL).

(viii) **GMA-8** : PEG-600 pseudocrown ether

A sample of GMA polymer beads (500 mL, <300 μm) was combined with molten PEG-600 (A.R., 750 mL) and stirred under dry nitrogen gas while heating to ~110°C for 9 hours. The mixture was cooled to ca. 80°C and filtered on a Buchner funnel, then the solids washed with toluene (2 x 200 mL). The product was then stirred with toluene (500 mL) to dissolve traces of PEG, filtered over a Büchner funnel, and the polymer washed again by the same process. Residual toluene was removed and the resin dried by heating in a vacuum oven. The toluene and PEG were recovered by rotary evaporation, and used for the preparation of two more batches (2 x 500 mL) of GMA-8 resin.

(ix) **GMA-9** : PEG-400 pseudocrown ether

A sample of sodium hydride (60%, 3.1 g, 78 mmol) was weighed into a flask and flushed with nitrogen. Two aliquots of petroleum ether (60-90°C fraction) were successively injected in, stirred thoroughly by a

teflon-coated stir bar, and drained off via syringe. The oil-free NaH remaining was suspended in anhydrous 1,4-dioxane (75 mL) as PEG-400 (15.0 g, 37.5 mmol) was added dropwise over 30 minutes, and the residues washed in with dioxane (5 mL). Small bubbles of gas were slowly evolved over several hours, so this mixture left to stir overnight. Meanwhile, GMA beads (60 mL, ≥300 μm) were left to stand and swell in anhydrous dioxane (200 mL). After 16 hours, the brown solution of PEG-400 disodium salt (containing some tan coloured viscous material) was quickly added to the stirring suspension of GMA in dioxane under nitrogen, washing in residues with more dioxane (10 mL). This mixture was stirred at room temperature for 2 hours, then heated to 100°C (reflux) for 1 hour. The mixture was allowed to cool before it was quenched by the addition of ammonium chloride (10.0 g, 187 mmol). The pale pinkish polymer was filtered off and washed with methanol (250 mL), then water (5 x 300 mL).

4.5 Solid Copolymer Products

(i) **CMA-1** : tris(2-aminoethyl)amine poly(methacrylamide)

(a) In a R/B flask, a batch of CMA pellets (100 mL) was added to tris(2-aminoethyl)amine (100 mL). This mixture was stirred with a teflon-coated magnetic stir-bar and heated in a sand bath to 160°C (± 5°C) under a blanket of dry nitrogen. The stirring mechanism ceased to operate less than two hours after the maximum temperature was attained, the viscous mixture having the colour of molasses. This was cooled and the flask washed out with tetrahydrofuran (THF, 5 x 250 mL) and then toluene (3 x 250 mL) over several days. Approximately one third of the mixture remained as insoluble residues at the bottom of the flask.

The viscous yellow solution of polymer in THF/toluene was concentrated to ca. 500 mL by rotary evaporation. This solution was poured into a rapidly stirring solution of HCl (10%, 100 mL) in d.i. water (1.5 L), forming fluffy white strands. This material was filtered off and slowly washed with aqueous NaOH (0.2 M, 1.7 L), then again with water (2 x 1.0 L). The resulting white material, with the appearance and consistency of soggy cotton wool, yellowed slightly when left to air-dry in a fume hood over a weekend. The cotton-like polymeric material was then dried in a vacuum oven for three days, recovering a mixture of water, toluene and tetrahydrofuran.

(b) The portion of the reaction mixture above which did not dissolve in the THF/toluene mixture was air-dried over several days. This was frozen in liquid nitrogen and smashed into small fragments using a mortar and pestle, then stirred with hydrochloric acid (6M, 150 mL) for one hour and rinsed with water (300 mL). The product consisted of white to amber-coloured chips of hard polymeric material (ca. 0.1 - 50 mm).

(ii) **CMA-2** : PEG-400 poly(methacrylate) pseudocrown ether

Two clean, dry, flexible PVC jar lids (6 cm diameter, 5 mm deep) were filled with a suspension of pulverised dibenzoyl peroxide (0.761 g, 3.1 mmol) in PEG-400 dimethacrylate (20.785 g, 38.8 mmol). These samples were topped with a quartz sheet, and irradiated using a high intensity UV lamp under dry nitrogen for one hour. After this time, it was noted that the material in the trays had formed some bubbles, which had set into the solid polymer (as had some crystals of peroxide catalyst). The discs were turned over, and irradiated on the other face for one hour. The samples were then immersed in water (1.0 L) for several days, during which time the intact solid discs fragmented into pieces ca. 1-10 mm

across. These fragments were filtered off and cryogenically ground, then sieved over an 800 μm mesh screen and flushed through several times with water. The larger fragments (ca. 25 mL) were washed with d.i. water (4 x 500 mL), and sent to Geo2, whereas the fines were retained for analysis. A sample of the fines was examined between two glass slides under magnification, and heated to 220°C at 10°C per minute. Although some moisture was apparently released at ~100°C, no softening or decomposition was observed. Elemental analysis of the anhydrous material gave 53.90% C and 8.35% H.

(iii) CMA-3 : PEG-600 poly(methacrylate) pseudocrown ether

A sample of CMA pellets (100 mL, 72.017 g) was stirred with molten PEG-600 (ca. 40°C, 167.474 g, 279.1 mmol) as pulverised anhydrous lithium iodide (0.117 g, 0.87 mmol) was added. The flask was fitted with a condenser, overhead stirrer, heating mantle, dry nitrogen gas inlet, and a low condenser side-arm to allow then escape of methanol. The mixture was then slowly heated to 200 °C (± 10°C) over 3 hours, and held at this temperature for 3 hours. The mixture became a homogeneous tan colour, with some distillate collecting in the lower condenser. The viscosity of the mixture had increased significantly when heating was discontinued.

The translucent tan rubbery solid, which was removed from the apparatus with a scalpel and tweezers. The fragments were soaked in water (800 mL) for several days, then the turbid aqueous solution decanted. This was repeated several times. The solid fragments that remained varied in colouration from a dark translucent red-brown to a pale translucent yellow, with some clear soft fragments and some opaque brittle white pieces. The entire batch was frozen under liquid nitrogen and cryogenically ground; the finest particles were removed via

countercurrent flotation over 30 minutes. The remainder (0.5 - 5.0 mm; ca. 100 mL) was washed with water (5 x 200 mL) and the fines retained for analysis. The anhydrous material was found to contain 57.41% C and 8.75% H.

(iv) **PUR-1** : PEG-600 polyurethane pseudocrown ether

(a) A batch of anhydrous PEG-600 (10.024 g, 16.7 mmol) was placed in a dry flask, and dichloromethane (25 mL) was distilled in from over active P_2O_5 under dry nitrogen. One drop of tin(II) 2-ethylhexanoate (catalyst) was added and mixed in. Tolylene 2,4-di-isocyanate (TDI) was melted in a bath of warm water, and then a sample (4.80 mL, 33.5 mmol) was pipetted out under nitrogen. This was dissolved in freshly distilled DCM (25 mL), and the PEG-600 solution prepared above was added dropwise over 3 hours, with stirring under dry nitrogen. The solution became somewhat warm, and was sealed after cooling for overnight storage at room temperature.

This solution was poured into a high-walled glass dish, covering the nine strips of vacuum-dried Nylon 6-6 (50 x 10 x 2 mm) on the bottom. The dish was covered by a glass lid, and left to stand over a weekend. This allowed ambient moisture to cure the unreacted isocyanate groups, and time for most of the solvent to evaporate. The clear, flexible rubbery sheet that resulted was dissected with a scalpel to remove the nylon strips, each with ca. 2 mm of clear coating. All the pieces were allowed to stand in water (2 x 800 mL) for 12 hours to cure residual isocyanate and to wash off unreacted PEG-600.

(b) Dichloromethane (25 mL) was distilled from over active P_2O_5 into a flask holding anhydrous PEG-600 (20.037 g, 33.4 mmol). This was

transferred to a pressure-equalising dropping funnel, and 6 drops of tin(II) ethylhexanoate were added. This was connected above another flask containing a magnetic flea, TDI (9.60 mL, 66.9 mmol) and freshly distilled DCM (25 mL),.

The PEG solution was added dropwise to the TDI solution, with vigorous stirring under a nitrogen atmosphere. The addition was completed over two hours, with the flask becoming warm. The mixture was stirred overnight before pouring the entire batch onto a 20 cm glass dish. This was left to cure in moist air in a fume hood overnight, producing a clear rubbery sheet with a number of bubbles entrained within it. This was washed with excess water, and the rubbery disc left to cure fully for several days in a fume hood.

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Appendix I

Infra-Red Spectra of Resin Products

Figure I(a) FTIR Spectrum of GMA Resin Beads (As Supplied)

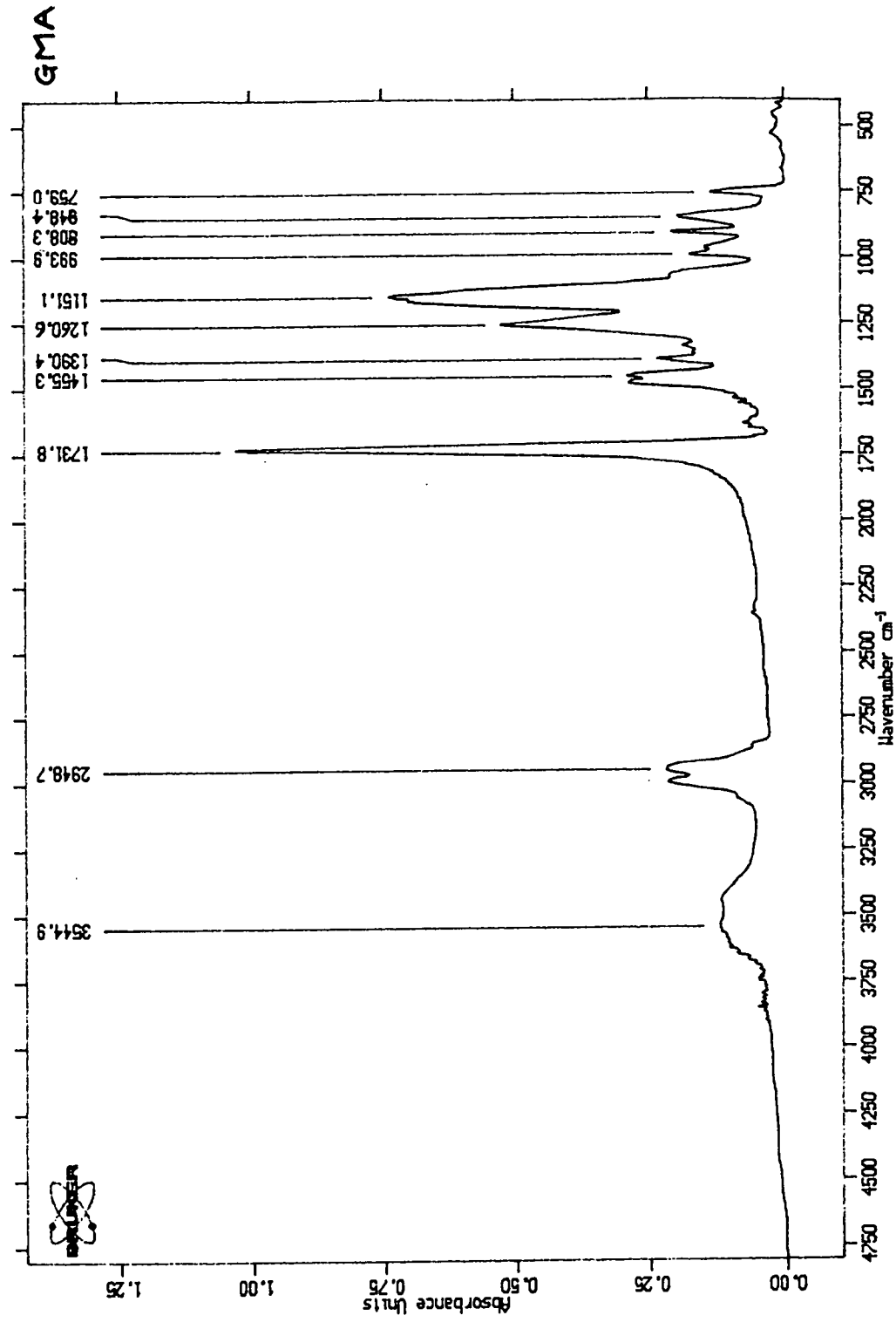


Figure I(b) FTIR Spectrum of PUR-1 Polyurethane Product

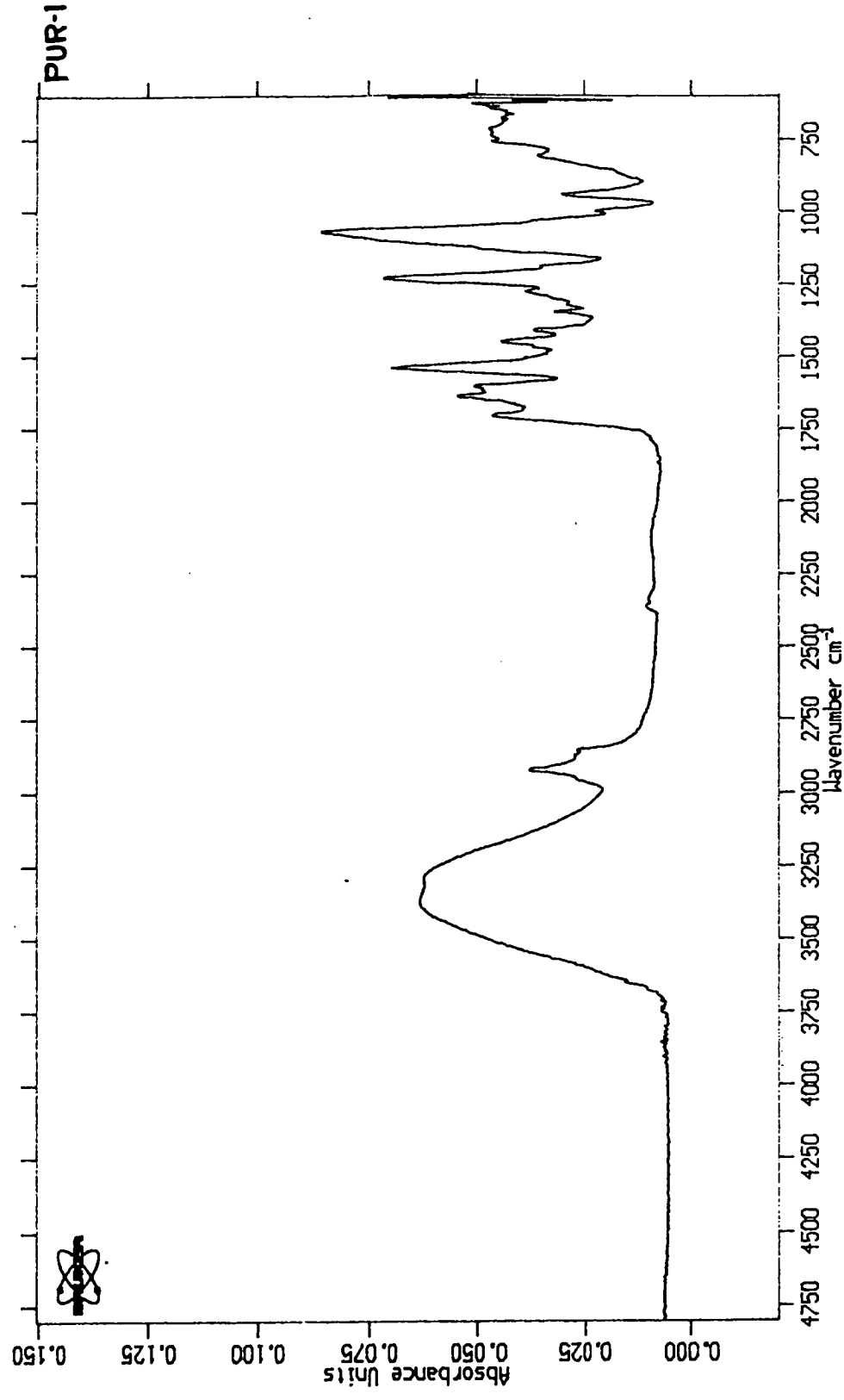


Figure I(c) FTIR Spectrum of PEG-400 Poly(methacrylate) CMA-2

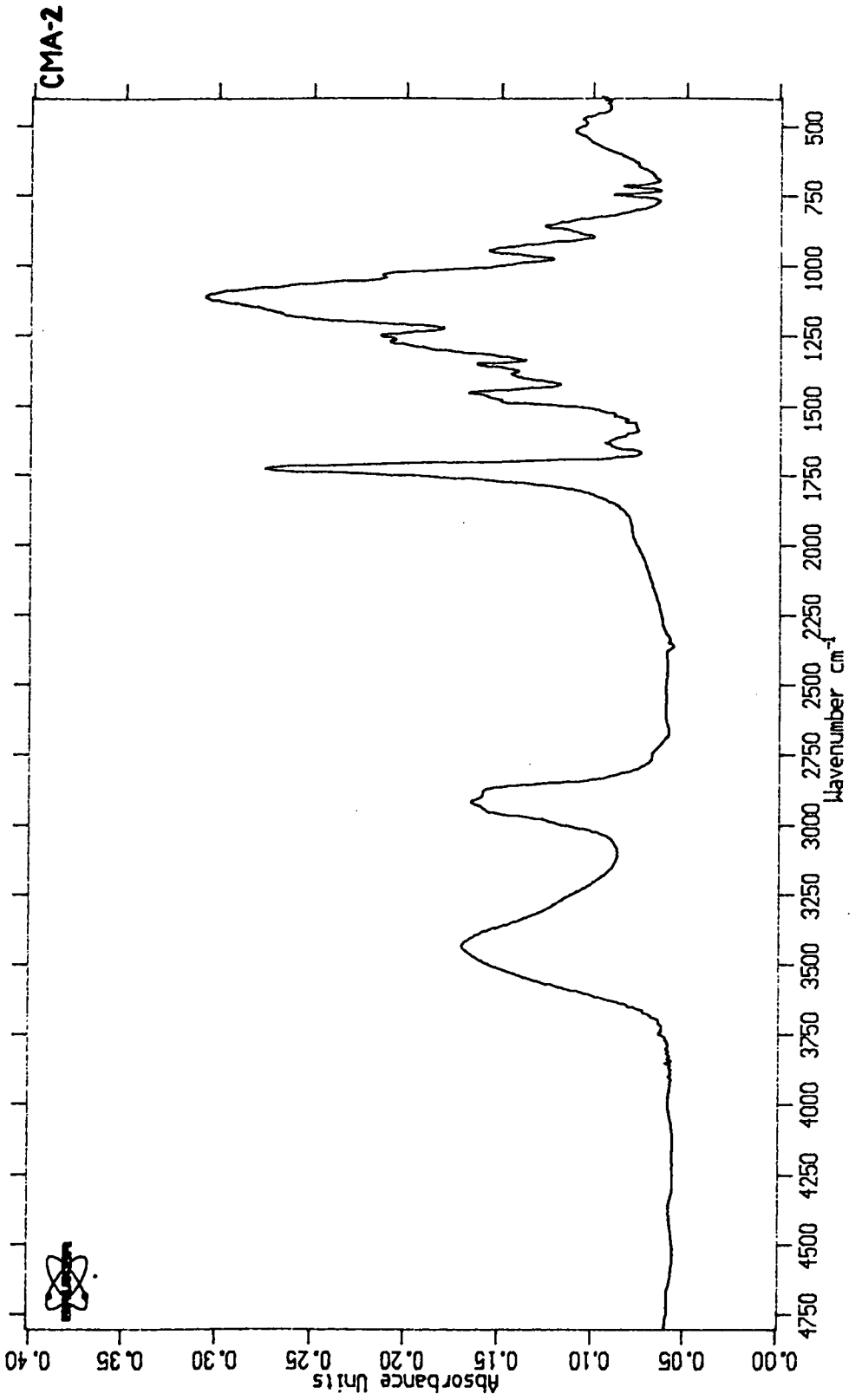


Figure I(d) FTIR Spectrum of PEG-600 Transesterified CMA-3

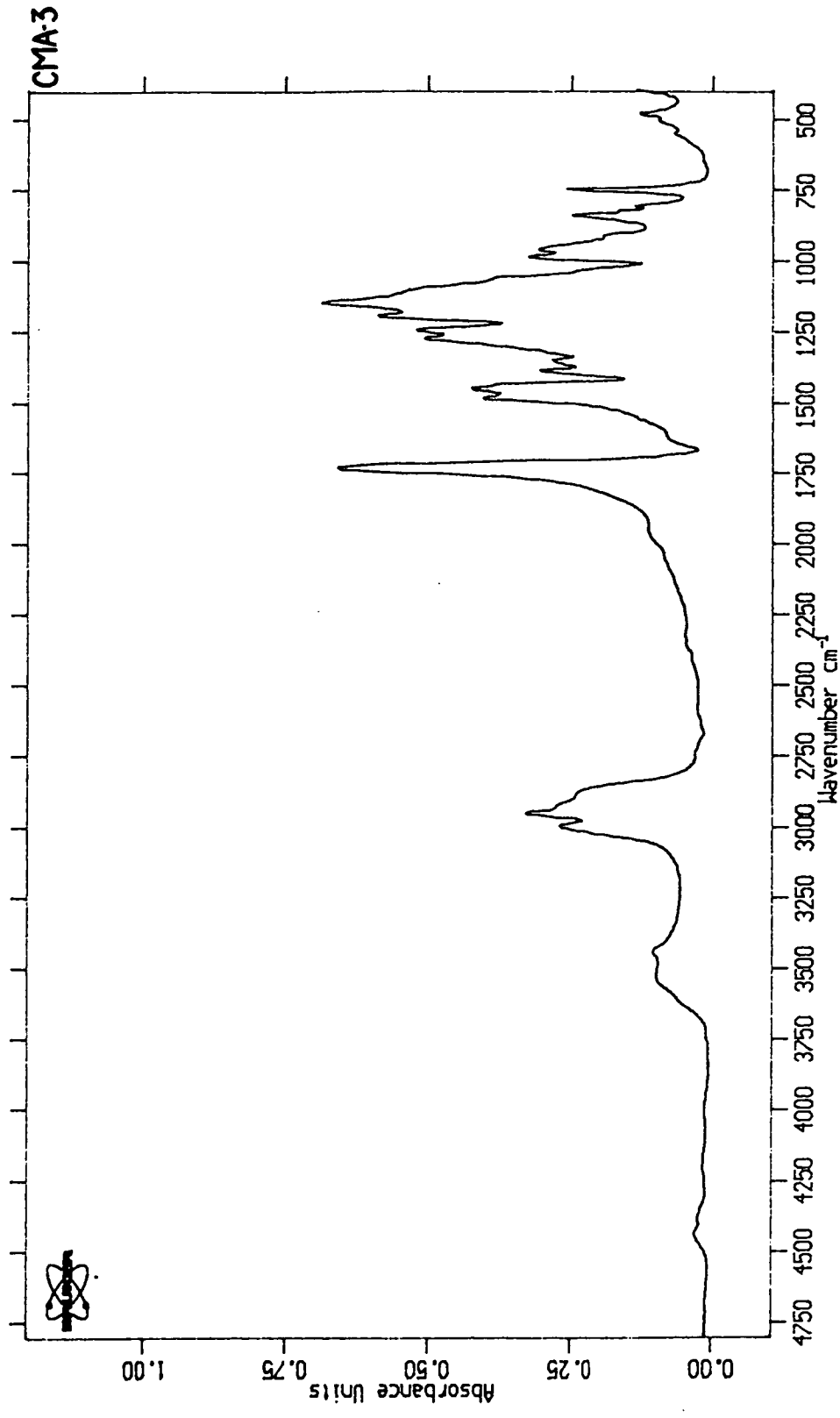
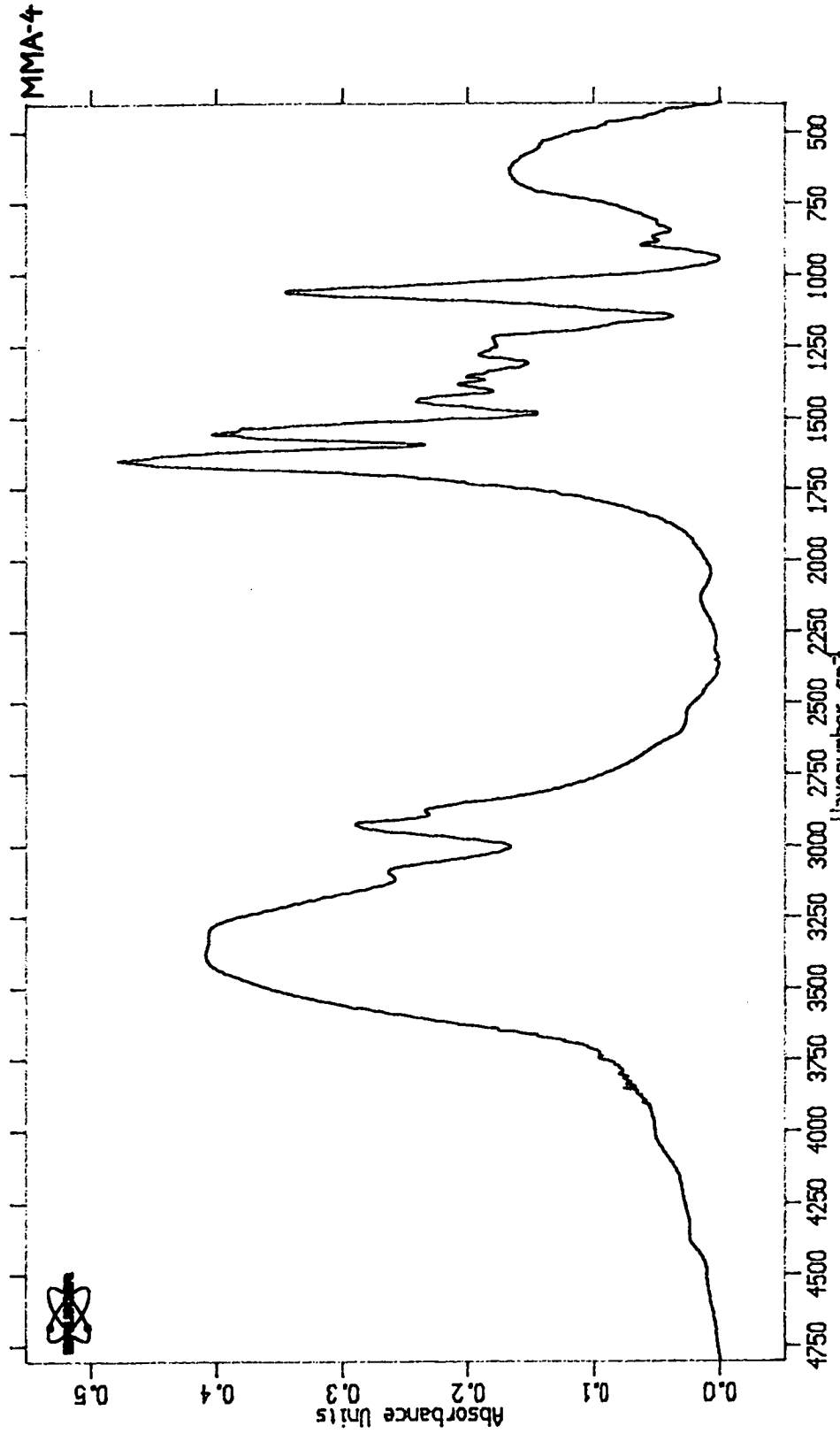


Figure I(e) FTIR Spectrum of Ethanolamide Product MMA-4



Appendix II

Microphotographs of Resin Products

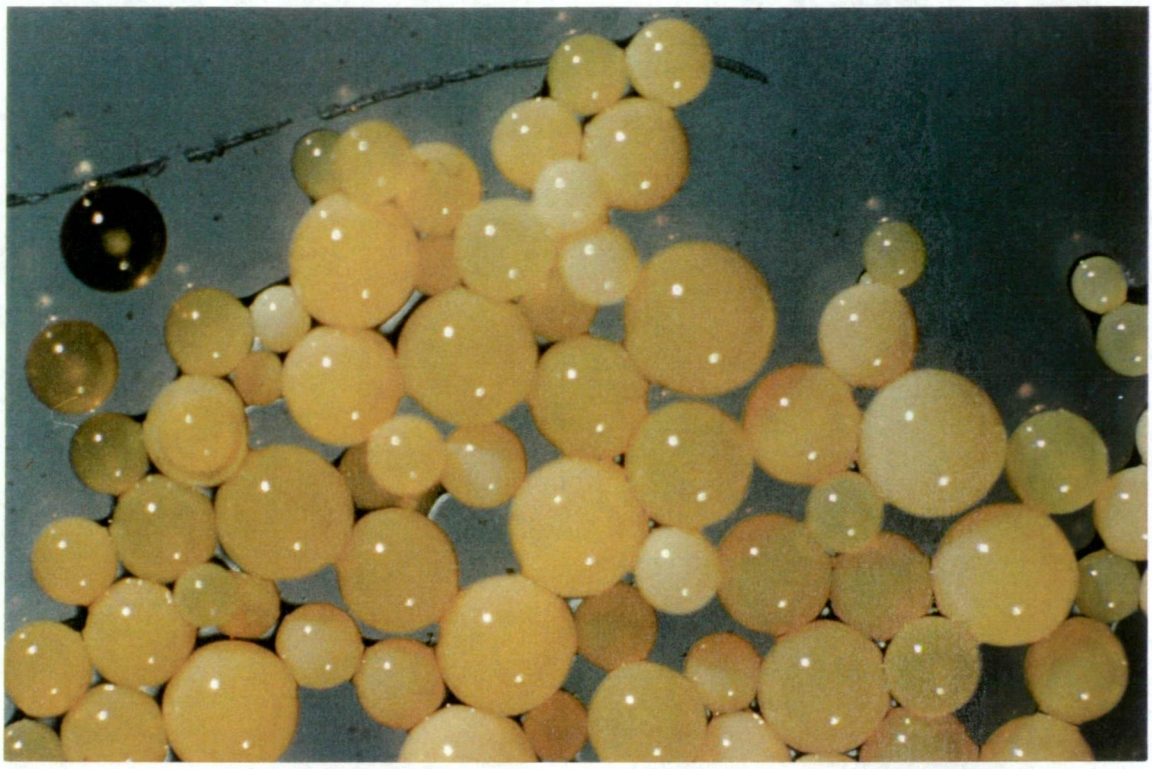


Figure II(a) Hydrated DMA Resin Beads (Free-Base, As Supplied)

Figure II(b) Enlargement of DMA Resin Beads, Illustrating 'Skin'

Figure II(c) Moist DMA-1 Resin Bead Product (HCl-form)

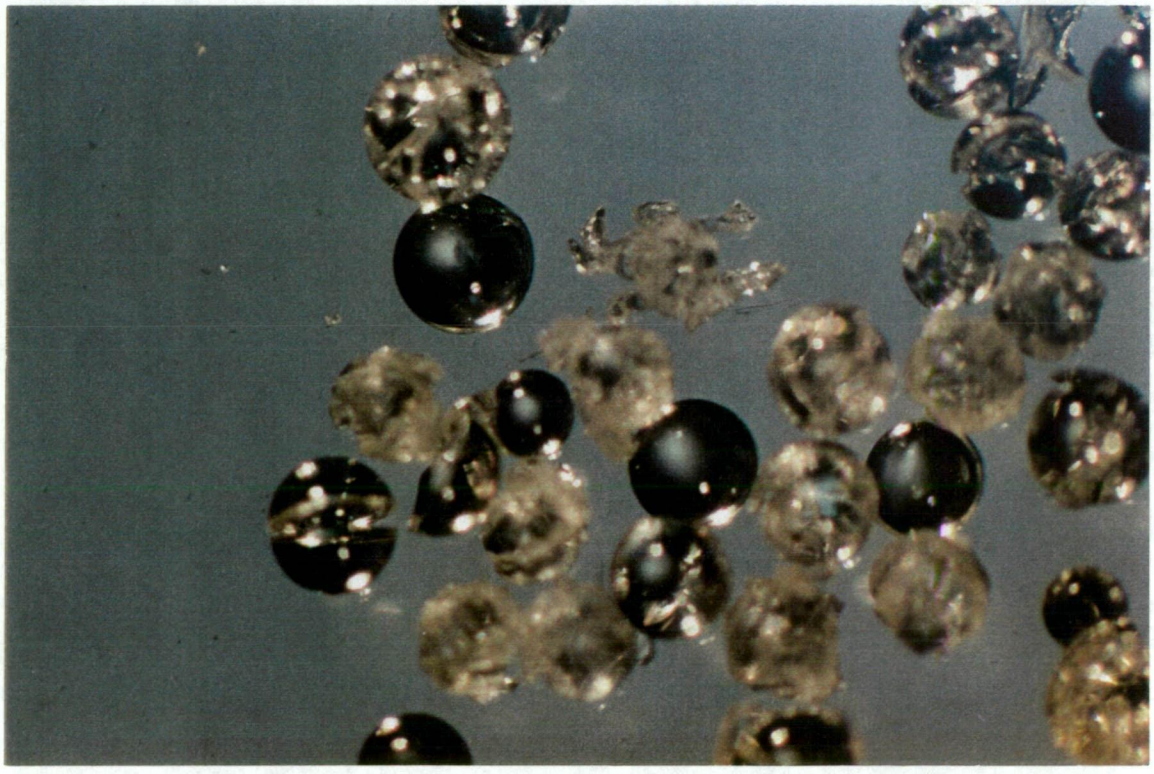


Figure II(d) Wet MMA-1 Resin Beads (HCl-form)

Figure II(e) Close-up of MMA-1 Beads, Illustrating Deformities

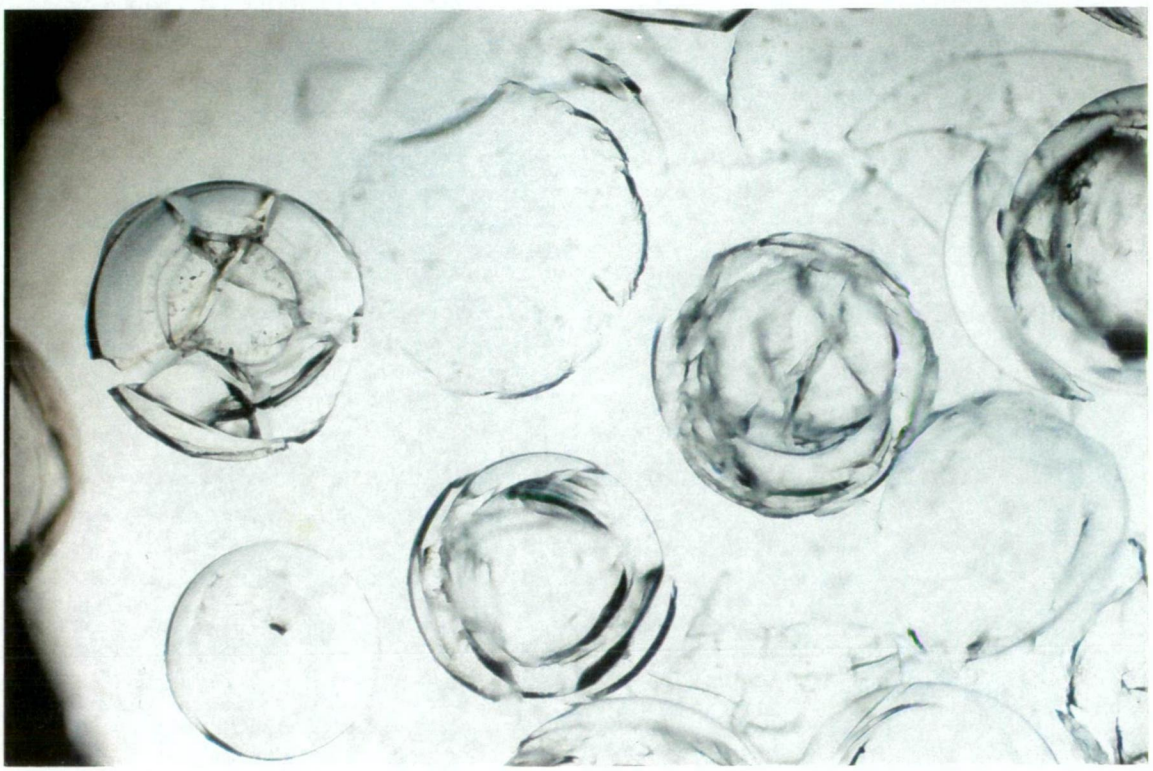
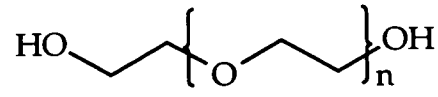


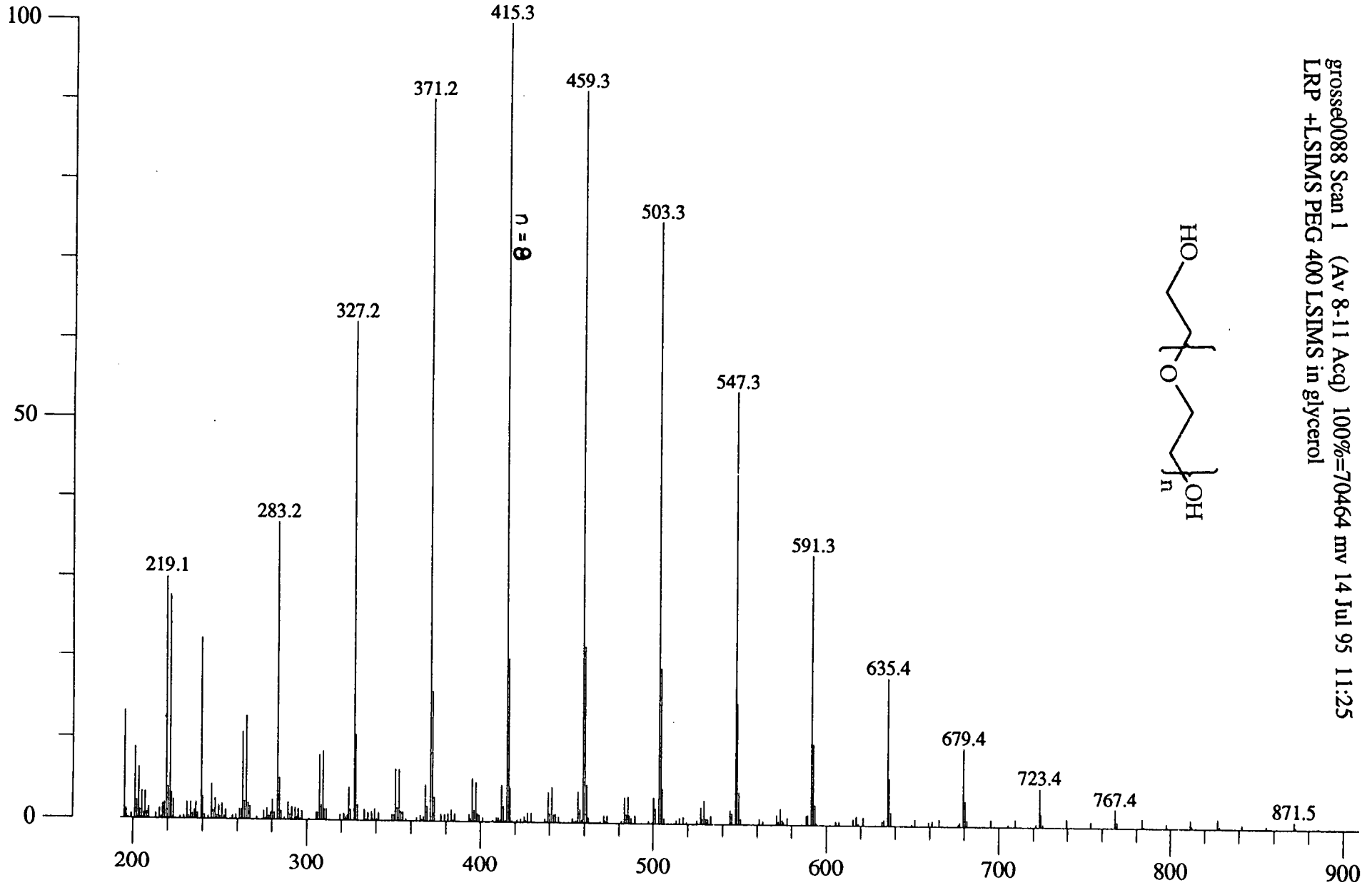
Figure II(f) MMA-1 Resin Beads, Shattered by Osmotic Shock

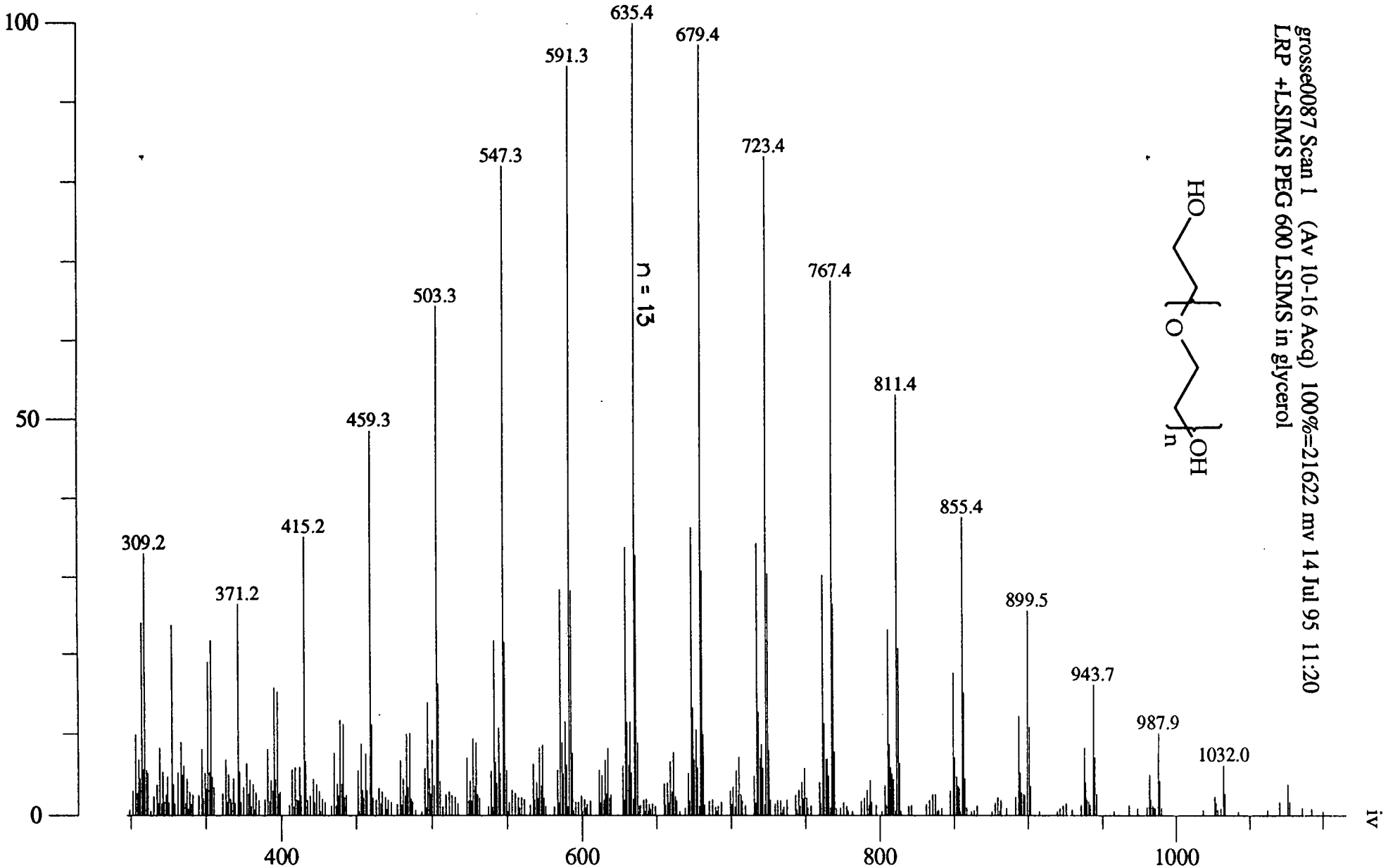
Appendix III

GC/MS & LSIMS of Synthesised Reagents

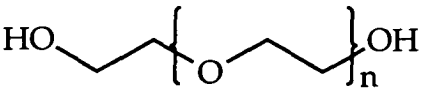
grosse0090 Scan 1 (Av 3, 3 Acq) 100%=119596 mv 14 Jul 95 11:34
LRP +LSIMS PEG 200 LSIMS neat



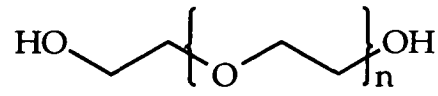

grosse0088 Scan 1 (Av 8-11 Acq) 100%=70464 mv 14 Jul 95 11:25
LRP +LSIMS PEG 400 LSIMS in glycerol
100
50
0
200
300
400
500
600
700
800
900
219.1
283.2
327.2
371.2
415.3
459.3
503.3
547.3
591.3
635.4
679.4
723.4
767.4
871.5
n = 8
HO
O
n
OH

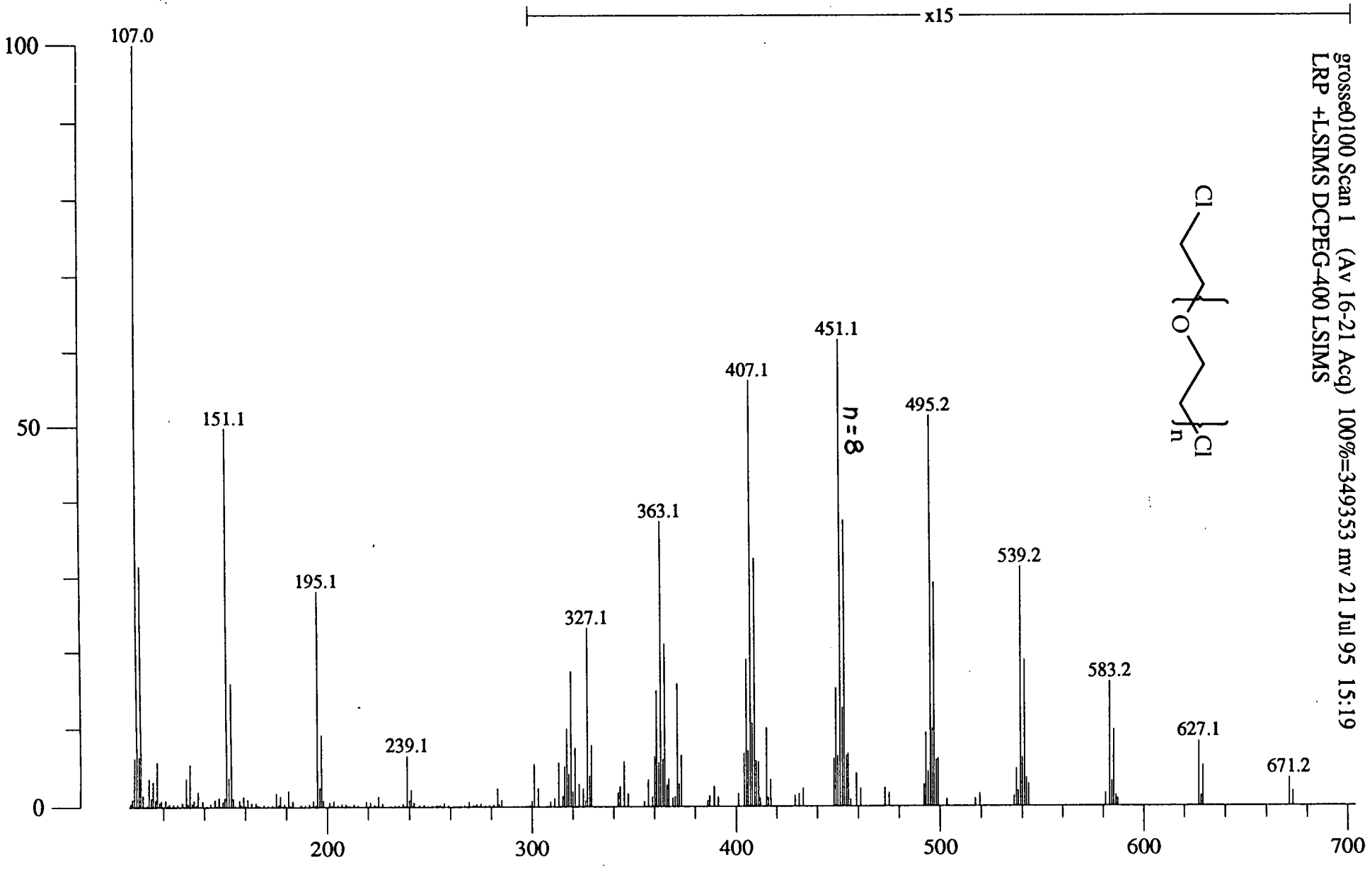

grosse0087 Scan 1 (Av 10-16 Acq) 100%=21622 mv 14 Jul 95 11:20
LRP +LSIMS PEG 600 LSIMS in glycerol
100
50
0
400
600
800
1000
309.2
371.2
415.2
459.3
503.3
547.3
591.3
635.4
679.4
723.4
767.4
811.4
855.4
899.5
943.7
987.9
1032.0
n = 13
HO
O
n
OH

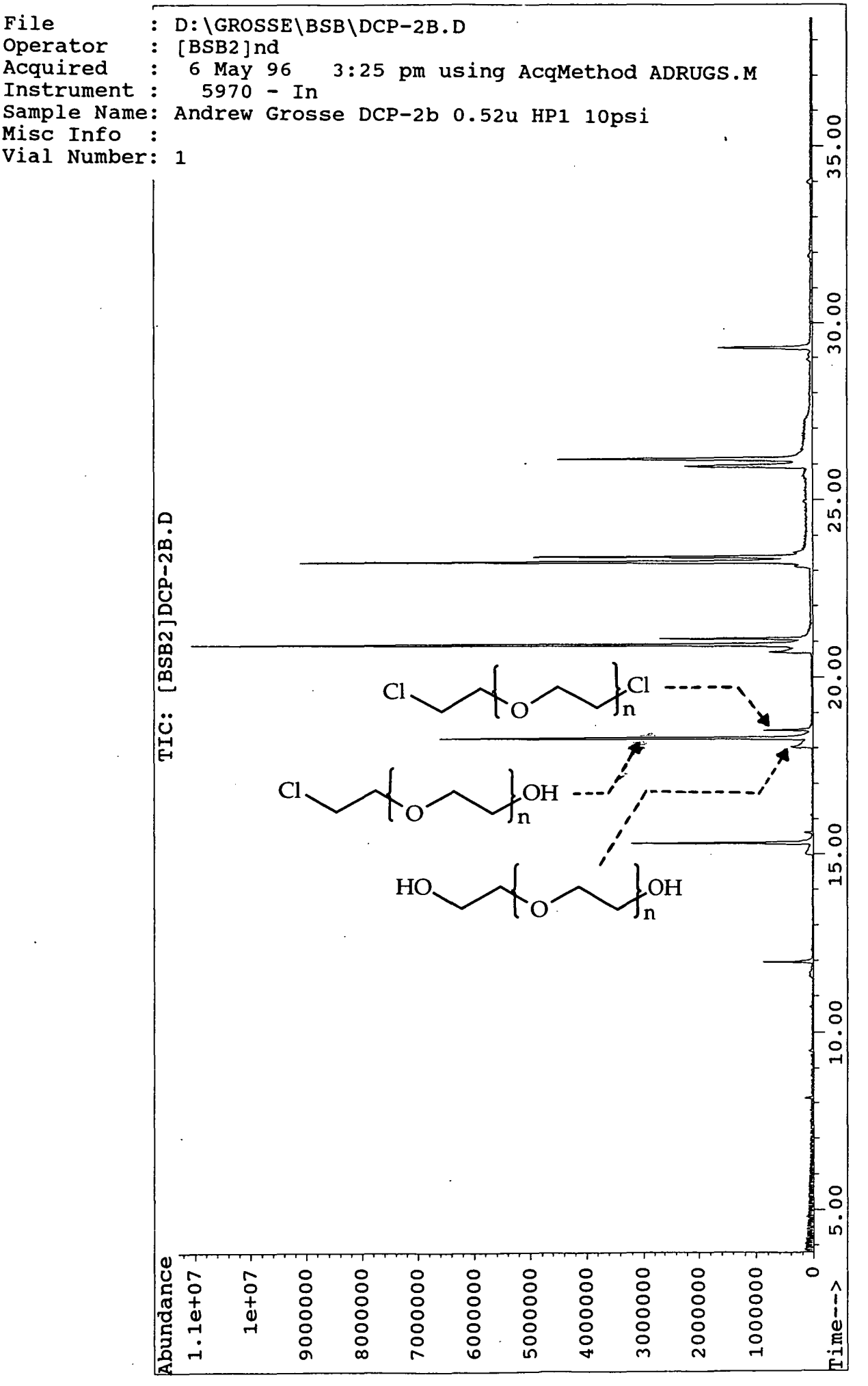
grosse0089 Scan 1 (Av 12-19 Acq) 100%=14896 mv 14 Jul 95 11:30
LRP +LSIMS PEG 900 LSIMS in glycerol



grosse0091 Scan 1 (Av 10-17 Acq) 100%=16867 mv 14 Jul 95 11:38
LRP +LSIMS PEG 1000 LSIMS in glycerol




x15
100
50
0
107.0
151.1
195.1
239.1
327.1
363.1
407.1
451.1
n=8
495.2
539.2
583.2
627.1
671.2
200
300
400
500
600
700
Cl
O
n
Cl
grosse0100 Scan 1 (Av 16-21 Acq) 100%=349353 mv 21 Jul 95 15:19
LRP +LSIMS DCPEG-400 LSIMS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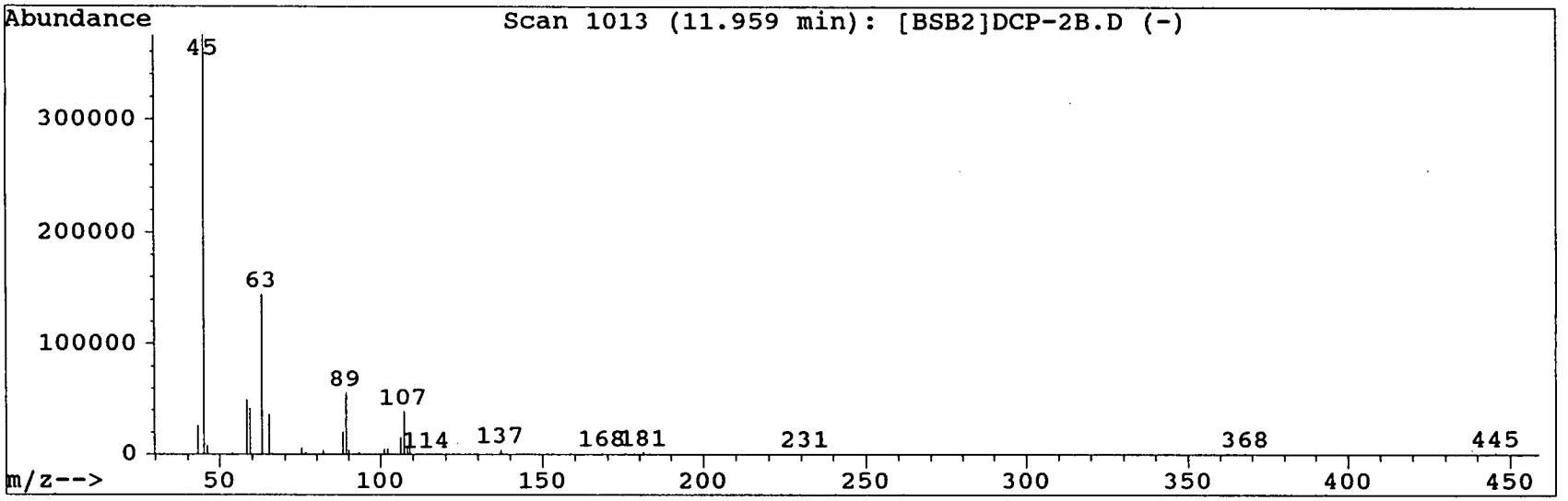
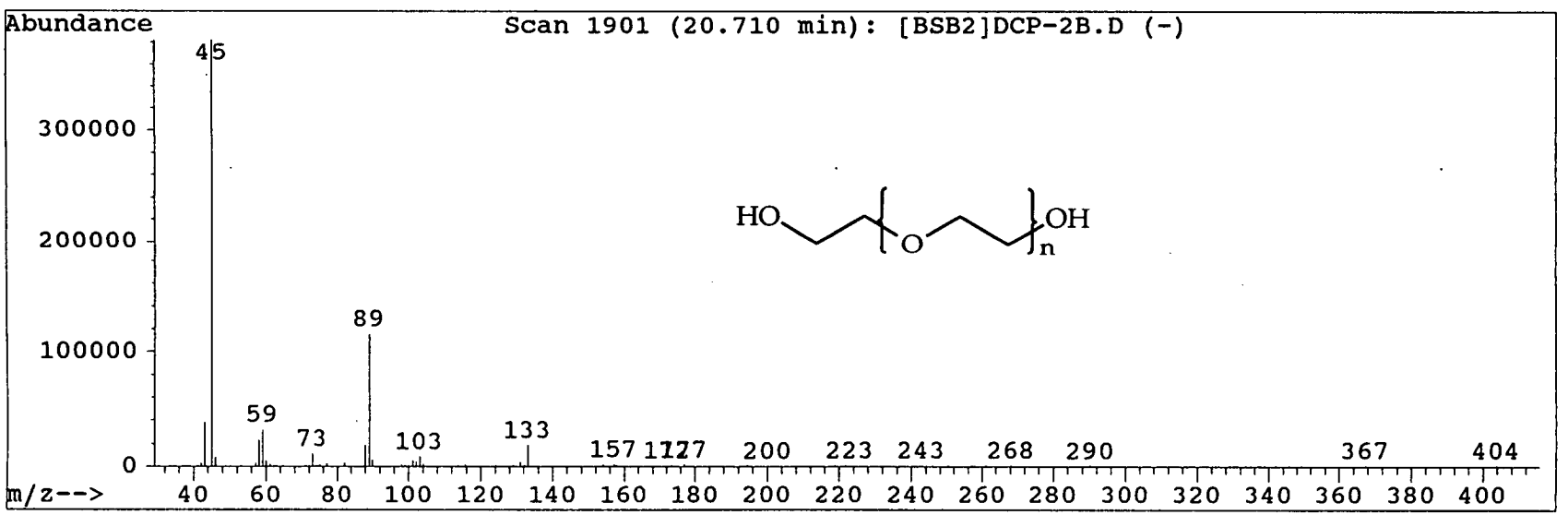
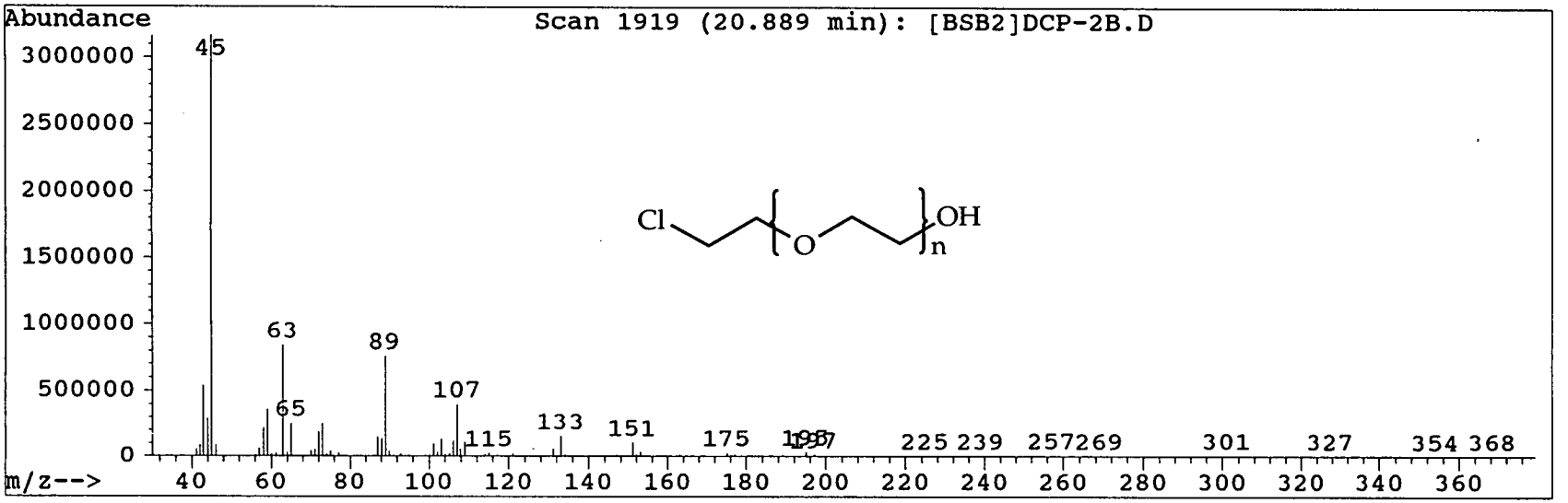
Operator : [BSB2]nd
Acquired : 6 May 96 3:25 pm using AcqMethod ADRUGS.M
Instrument : 5970 - In
Sample Name: Andrew Grosse DCP-2b 0.52u HP1 10psi
Misc Info :
Vial Number: 1
TIC: [BSB2]DCP-2B.D
Abundance
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
35.00
Cl
O
n
Cl
OH
HO


Abundance
Scan 1013 (11.959 min): [BSB2]DCP-2B.D (-)
45
300000
200000
63
100000
89
107
0
114
137
168
181
231
368
445
m/z-->
50
100
150
200
250
300
350
400
450


Abundance
Scan 1901 (20.710 min): [BSB2]DCP-2B.D (-)
45
300000
200000
89
100000
59
73
103
133
157
177
0
200
223
243
268
290
367
404
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
HO
O
n
OH


Abundance
Scan 1919 (20.889 min): [BSB2]DCP-2B.D
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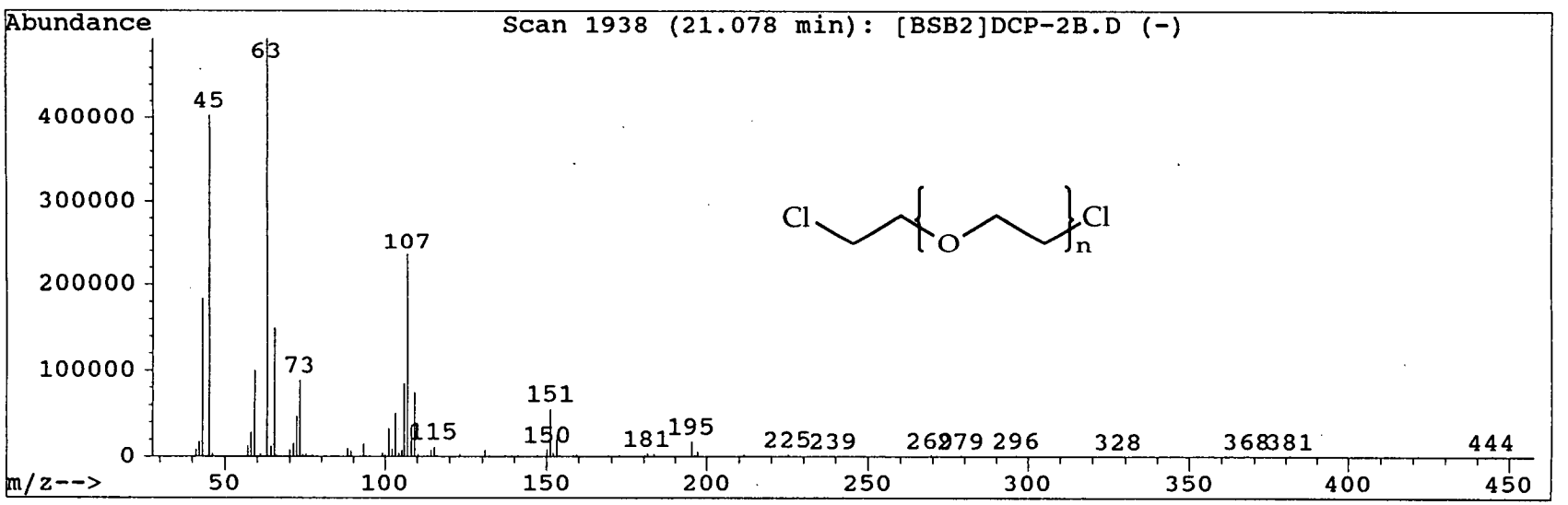
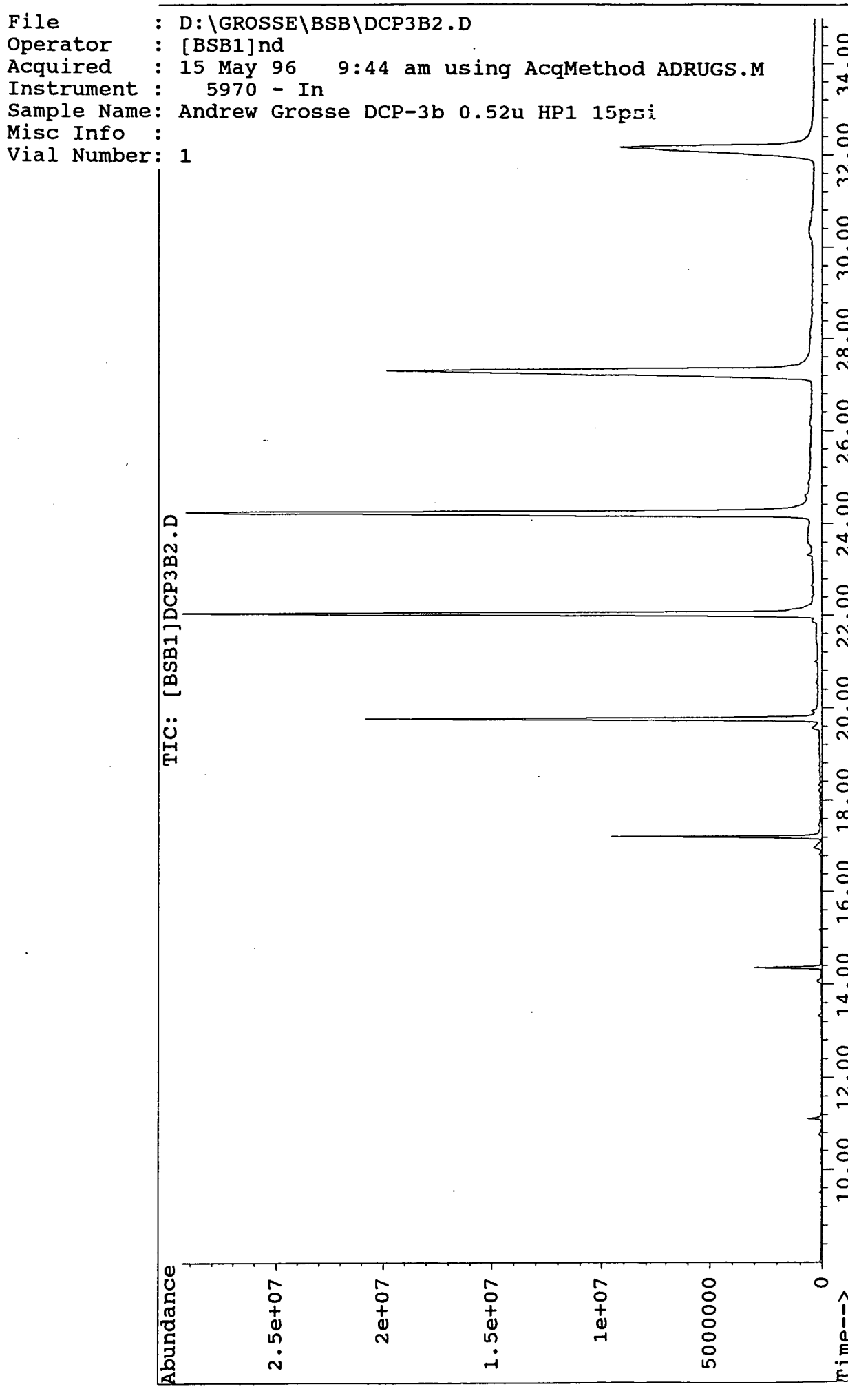
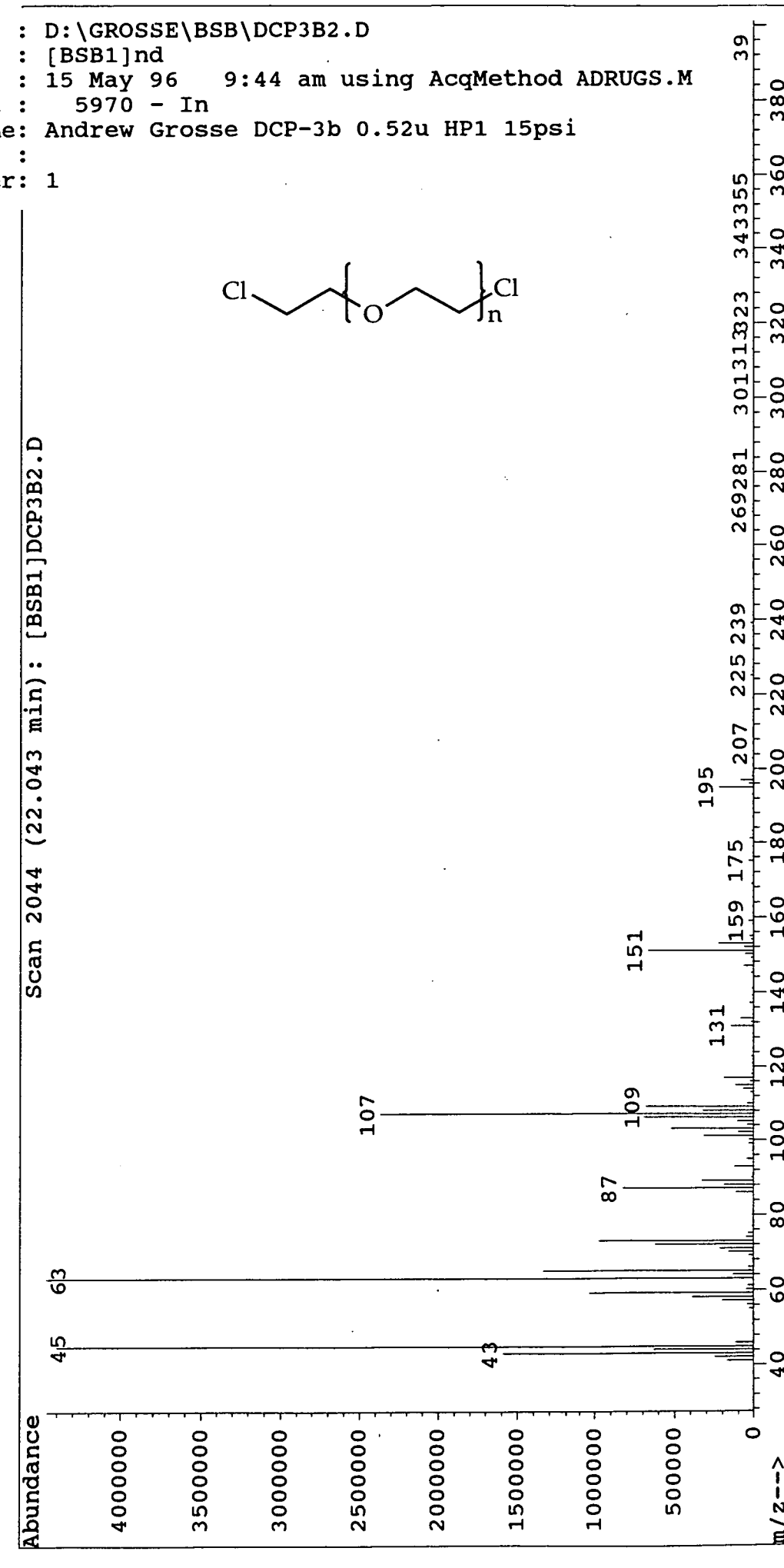
2500000
2000000
1500000
1000000
500000
0
45
63
89
65
107
115
133
151
175
225 239 257269
301
327
354 368
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360
Cl
O
n
OH


Abundance
Scan 1938 (21.078 min): [BSB2]DCP-2B.D (-)
400000
300000
200000
100000
0
63
45
107
73
151
115
150
181
195
225239
262
279 296
328
368381
444
m/z-->
50 100 150 200 250 300 350 400 450
Cl
O
n
Cl


File : D:\GROSSE\BSB\DCP3B2.D
Operator : [BSB1]nd
Acquired : 15 May 96 9:44 am using AcqMethod ADRUGS.M
Instrument : 5970 - In
Sample Name: Andrew Grosse DCP-3b 0.52u HP1 15psi
Misc Info :
Vial Number: 1
TIC: [BSB1]DCP3B2.D
Abundance
2.5e+07
2e+07
1.5e+07
1e+07
5000000
0
Time-->
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
32.00
34.00

File : D:\GROSSE\BSB\DCP3B2.D
Operator : [BSB1]nd
Acquired : 15 May 96 9:44 am using AcqMethod ADRUGS.M
Instrument : 5970 - In
Sample Name: Andrew Grosse DCP-3b 0.52u HP1 15psi
Misc Info :
Vial Number: 1



Appendix IV

Cu(II) Isotherm Data and AAS Results

	Resin	[Head] ppm	[liquor] ppm	[difference]	ug on resin	Resin Mass	[resin] ppm	Time (hrs)
1	MA-005	73.965	73.59	0.375	37.5	4.493	8.35	1
2	MA-005	73.965	73.83	0.135	13.5	4.493	3.00	2
3	MA-005	74.53	74.04	0.49	49	4.493	10.91	4
4	MA-005	74.94	74.89	0.05	5	4.493	1.11	8
5	MA-005	76.715	75.89	0.825	82.5	4.493	18.36	25
6	MA-007	73.965	58.58	15.385	1538.5	4.743	324.37	1
7	MA-007	73.965	48.72	25.245	2524.5	4.743	532.26	2
8	MA-007	74.53	37.84	36.69	3669	4.743	773.56	4
9	MA-007	74.94	26.89	48.05	4805	4.743	1013.07	8
10	MA-007	76.715	13.98	62.735	6273.5	4.743	1322.69	25
11	MA-008	73.965	72.71	1.255	125.5	5.222	24.03	1
12	MA-008	73.965	72.8	1.165	116.5	5.222	22.31	2
13	MA-008	74.53	73.4	1.13	113	5.222	21.64	4
14	MA-008	74.94	73.38	1.56	156	5.222	29.87	8
15	MA-008	76.715	73.26	3.455	345.5	5.222	66.16	25
16	MA-018	73.965	72.41	1.555	155.5	0.757	205.42	1
17	MA-018	73.965	72.2	1.765	176.5	0.757	233.16	2
18	MA-018	74.53	72.82	1.71	171	0.757	225.89	4
19	MA-018	74.94	72.49	2.45	245	0.757	323.65	8
20	MA-018	76.715	74.96	1.755	175.5	0.757	231.84	25
21	MA-027	73.965	69.79	4.175	417.5	3.388	123.23	1
22	MA-027	73.965	68.11	5.855	585.5	3.388	172.82	2
23	MA-027	74.53	67.35	7.18	718	3.388	211.92	4
24	MA-027	74.94	66.01	8.93	893	3.388	263.58	8
25	MA-027	76.715	66.38	10.335	1033.5	3.388	305.05	25
26	PS-010	73.965	65.01	8.955	895.5	4.114	217.67	1
27	PS-010	73.965	58.45	15.515	1551.5	4.114	377.13	2

	Resin	[Head] ppm	[liquor] ppm	[difference]	ug on resin	Resin Mass	[resin] ppm	Time (hrs)
28	PS-010	74.53	50.29	24.24	2424	4.114	589.21	4
29	PS-010	74.94	41.06	33.88	3388	4.114	823.53	8
30	PS-010	76.715	33.58	43.135	4313.5	4.114	1048.49	25
31	PS-026	73.965	72.56	1.405	140.5	4.1	34.27	1
32	PS-026	73.965	72.47	1.495	149.5	4.1	36.46	2
33	PS-026	74.53	72.34	2.19	219	4.1	53.41	4
34	PS-026	74.94	71.15	3.79	379	4.1	92.44	8
35	PS-026	76.715	72.73	3.985	398.5	4.1	97.20	25
36	PS-072	73.965	54.41	19.555	1955.5	4.032	485.00	1
37	PS-072	73.965	44.58	29.385	2938.5	4.032	728.79	2
38	PS-072	74.53	31.87	42.66	4266	4.032	1058.04	4
39	PS-072	74.94	19.88	55.06	5506	4.032	1365.58	8
40	PS-072	76.715	10.59	66.125	6612.5	4.032	1640.00	25
41	PS-073	73.965	60.92	13.045	1304.5	4.675	279.04	1
42	PS-073	73.965	52.99	20.975	2097.5	4.675	448.66	2
43	PS-073	74.53	42.78	31.75	3175	4.675	679.14	4
44	PS-073	74.94	32.62	42.32	4232	4.675	905.24	8
45	PS-073	76.715	26.04	50.675	5067.5	4.675	1083.96	25
46	PS-074	73.965	58.91	15.055	1505.5	4.628	325.30	1
47	PS-074	73.965	50.49	23.475	2347.5	4.628	507.24	2
48	PS-074	74.53	39.13	35.4	3540	4.628	764.91	4
49	PS-074	74.94	30.3	44.64	4464	4.628	964.56	8
50	PS-074	76.715	15.03	61.685	6168.5	4.628	1332.87	25
51	PS-088	73.965	71.56	2.405	240.5	4.356	55.21	1
52	PS-088	73.965	71.69	2.275	227.5	4.356	52.23	2
53	PS-088	74.53	71.08	3.45	345	4.356	79.20	4
54	PS-088	74.94	70.33	4.61	461	4.356	105.83	8
55	PS-088	76.715	71.15	5.565	556.5	4.356	127.75	25

	Resin	[Head Liquor]	[liquor] ppm	[difference]	ug on resin	Resin Mass	[resin] mg/kg
1	MA-005	10.28	10.1	0.18	18	4.493	4.01
2	MA-005	24.9	24.72	0.18	18	4.493	4.01
3	MA-005	56.54	55.97	0.57	57	4.493	12.69
4	MA-005	73.97	73.59	0.38	38	4.493	8.46
5	MA-005	0	0	0	0	4.493	0.00
6							
7	MA-007	10.28	5.598	4.682	468.2	4.743	98.71
8	MA-007	24.9	18.36	6.54	654	4.743	137.89
9	MA-007	56.54	42.29	14.25	1425	4.743	300.44
10	MA-007	73.97	48.72	25.245	2524.5	4.743	532.26
11	MA-007	0	0	0	0	4.743	0.00
12							
13	MA-008	10.28	10.13	0.15	15	5.222	2.87
14	MA-008	24.9	24.76	0.14	14	5.222	2.68
15	MA-008	49.72	49.28	0.44	44	5.222	8.43
16	MA-008	73.97	72.8	1.165	116.5	5.222	22.31
17	MA-008	0	0	0	0	5.222	0.00
18							
19	MA-018	10.28	9.833	0.447	44.7	0.757	59.05
20	MA-018	24.9	24.28	0.62	62	0.757	81.90
21	MA-018	49.72	48.34	1.38	138	0.757	182.30
22	MA-018	73.97	72.2	1.765	176.5	0.757	233.16
23	MA-018	0	0	0	0	0.757	0.00
24							

	Resin	[Head Liquor]	[liquor] ppm	[difference]	ug on resin	Resin Mass	[resin] mg/kg
25	MA-027	10.28	9.648	0.632	63.2	3.388	18.65
26	MA-027	24.9	23.24	1.66	166	3.388	49.00
27	MA-027	49.72	47.56	2.16	216	3.388	63.75
28	MA-027	73.97	68.11	5.855	585.5	3.388	172.82
29	MA-027	0	0	0	0	3.388	0.00
30							
31	PS-010	10.28	7.401	2.879	287.9	4.114	69.98
32	PS-010	24.9	20.06	4.84	484	4.114	117.65
33	PS-010	56.54	41.64	14.9	1490	4.114	362.18
34	PS-010	73.97	58.45	15.515	1515.5	4.114	377.13
35	PS-010	0	0	0	0	4.114	0.00
36							
37	PS-026	10.28	10.02	0.26	26	4.1	6.34
38	PS-026	24.9	24.42	0.48	48	4.1	11.71
39	PS-026	56.54	55.43	1.11	111	4.1	27.07
40	PS-026	73.97	72.34	2.19	219	4.1	53.41
41	PS-026	0	0	0	0	4.1	0.00
42							
43	PS-072	10.28	6.315	3.965	396.5	4.032	98.34
44	PS-072	24.9	17.95	6.95	695	4.032	172.37
45	PS-072	49.72	28.06	21.66	2166	4.032	537.20
46	PS-072	73.97	44.58	29.385	2938.5	4.032	728.79
47	PS-072	0	0	0	0	4.032	0.00
48							

	Resin	[Head Liquor]	[liquor] ppm	[difference]	ug on resin	Resin Mass	[resin] mg/kg
49	PS-073	10.28	6.049	4.231	423.1	4.675	90.50
50	PS-073	24.9	19.26	5.64	564	4.675	120.64
51	PS-073	49.72	30.77	18.95	1895	4.675	405.35
52	PS-073	73.97	52.99	20.975	2097.5	4.675	448.66
53	PS-073	0	0	0	0	4.675	0.00
54							
55	PS-074	10.28	6.371	3.909	390.9	4.628	84.46
56	PS-074	24.9	18.24	6.66	666	4.628	143.91
57	PS-074	73.97	50.49	23.475	2347.5	4.628	507.24
58	PS-074	0	0	0	0	4.628	0.00
59	PS-074	99.39	72.92	26.47	2647	4.628	571.95
60							
61	PS-088	10.28	9.934	0.346	34.6	4.356	7.94
62	PS-088	24.9	24.28	0.62	62	4.356	14.23
63	PS-088	56.54	54.55	1.99	199	4.356	45.68
64	PS-088	73.97	71.56	2.405	240.5	4.356	55.21
65	PS-088	0	0	0	0	4.356	0.00

Appendix V

Schematic Diagram of 20 Litre Reaction Apparatus

(A) Schematic Diagram of Reactor

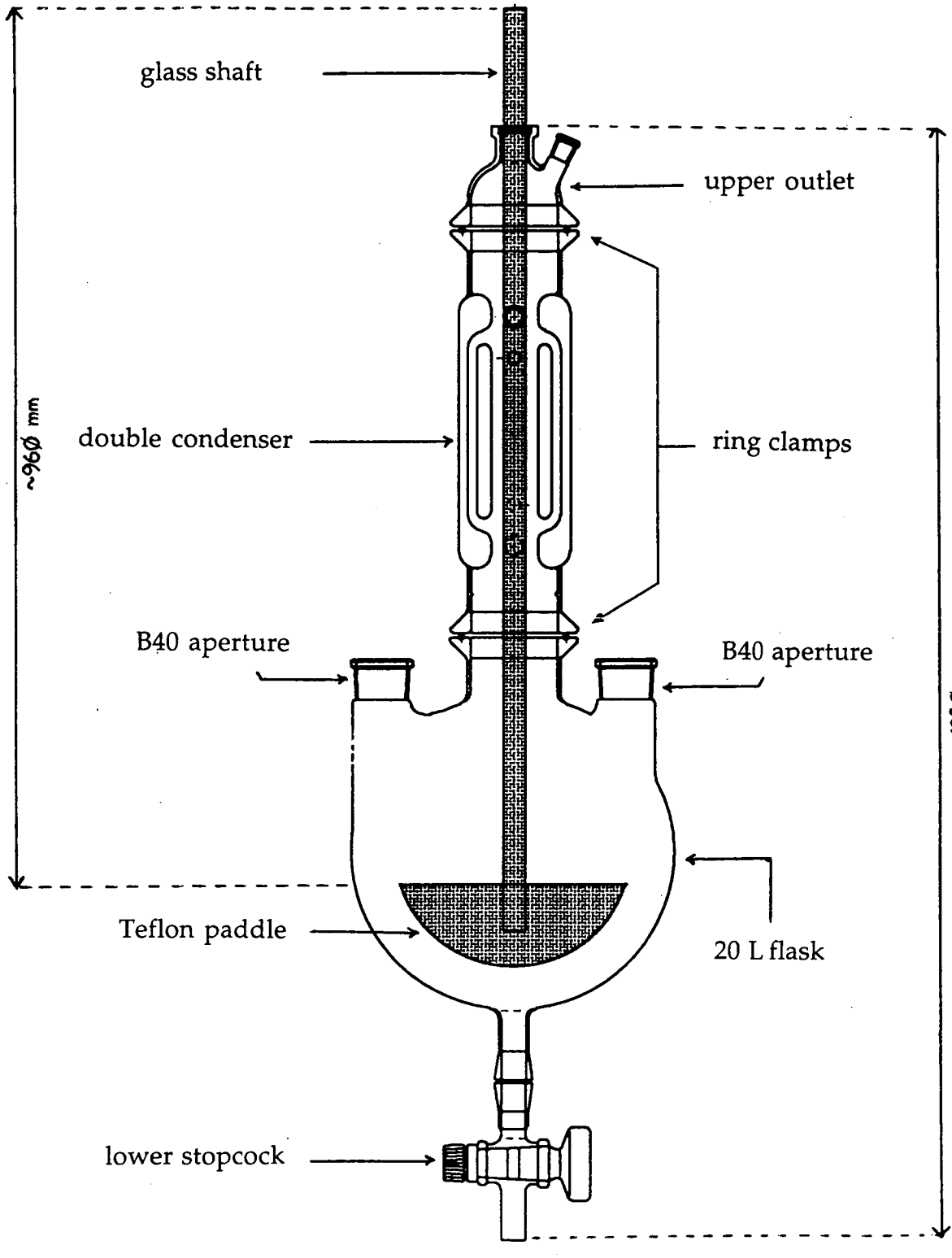


Diagram by Mike Brandon, Glassblower, UTAS

Appendix VI

Complete Resin List by Substrate

Resin Code	Moiety
CMS	*[precursor resin]* chloromethyl
CMS-1	tris(2-aminoethyl)amine
CMS-2	1°-amine
CMS-3	2°-ethylamine
CMS-4	2°-isopropylamine
CMS-5	*sym*-diethylenetriamine tetraacetic acid
CMS-6	aminodiacetic acid
CMS-7	*asym-* diethylenetriamine tetraacetic acid *[methanol]*
CMS-8	*asym-* diethylenetriamine tetraacetic acid *[1,4-dioxane]*
CMS-9	catechol
CMS-10	PEG-400 benzocrown
CMS-11	PEG-600 benzocrown
CMS-12	PEG-2000 pseudocrown
CMS-13	PEG-1500 pseudocrown
CMS-14	PEG-900 pseudocrown
CMS-15	PEG-600 pseudocrown
CMS-16	PEG-600 pseudocrown [toluene]
CMS-17	*[control treatment]* sodium methoxide in methanol
CMS-18	*[control treatment]* sodium methoxide in 1,4-dioxane
CMS-19	*[control treatment]* 32% HCl and methanol
CMS-20	triethylamine
CMS-21	diethylamine

Resin Code	Moiety
CMS-22	diethanolamine
CMS-23	*n*-octylamine
CMS-24	benzylamine
CMS-25	ethanolamine
CMS-26	butylamine
CMS-27	isopropylamine
DMA	*[precursor resin]* diethylenetriamine methacrylamide
DMA-1	*asym-* diethylenetriamine triacetic acid
GMA	*[precursor resin]* 2,3-epoxypropyl ester
GMA-1	tris(2-aminoethyl)amine
GMA-2	2,3-dihydroxypropyl ester
GMA-3	3-amino-2-hydroxypropyl ester
GMA-4	PEG-900 pseudocrown
GMA-5	PEG-200 pseudocrown
GMA-6	PEG-900 pseudocrown *[KOH hydrolysed]*
GMA-7	PEG-2000 pseudocrown
GMA-8	PEG-600 pseudocrown
GMA-9	PEG-400 pseudocrown *[dioxane]*
GMB	*[precursor resin]* large bead 2,3-epoxypropyl ester
GMB-1	PEG-900 pseudocrown
GMB-2	PEG-400 pseudocrown
GMB-3	PEG-600 pseudocrown

Resin Code	Moiety
MMA	*[precursor resin]* methyl ester
MMA-1	tris(2-aminoethyl)amine
MMA-2	mild alkaline hydrolysis
MMA-3	harsh alkaline hydrolysis
MMA-4	2-aminoethanol amide/ester
MMB	*[precursor resin]* large bead methyl ester
MMB-1	tris(2-aminoethyl)amine
MMB-2	harsh alkaline hydrolysis
MMC	*[precursor resin]* methyl ester
MMC-1	tris(2-aminoethyl)amine
CMA	*[precursor resin]* thermoplastic PMMA
CMA-1	tris(2-aminoethyl)amine
CMA-2	polymerised PEG-400 dimethacrylate
CMA-3	PMMA transesterified with PEG-600
PUR-1	polyurethane from PEG-600 + toluene 2,4-diisocyanate