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CHROMATOGRAPHY OF POLYCARBAMOYL SULPHONATES (ANIONIC POLYURETHANE DERIVATIVES)

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SUMMARY

The composition of some polyurethanes used to shrink-resist wool with a poly(propylene oxide) backbone and terminal $-NHCOSO_3^-Na^+$ groups, *i.e.* polycarbamoyl sulphonates (PCSs), have been investigated by chromatographic methods. The molecular weight distribution at different stages in the preparation of PCSs was examined by gel permeation chromatography (GPC) using detection methods appropriate to either the total polymer concentration or the number of terminal groups. Low-molecular-weight impurities in PCS preparations were investigated by GPC and reversed-phase liquid chromatography.

Problems in assigning PCS molecular weights on aqueous GPC on a surface modified silica column were resolved by the use of polystyrene gel columns and tetrahydrofuran eluent with either: (i) the conversion of the PCS to a urea derivative by reaction with di-*n*-butylamine, or (ii) changing the PCS counter ion from sodium to methyltrioctylammonium. The principle of the second method was also applied to some cationic polyurethane derivatives.

Reaction with 1-(2-pyridyl)piperazine converts carbamoyl sulphonates and isocyanates into derivatives with strong ultraviolet absorption at 300 nm. This derivatization reaction gives an estimate of the number of terminal carbamoyl sulphonate groups in the GPC fractions of a PCS, or terminal isocyanates in polyisocyanates. This method was the most sensitive way to estimate the bisulphite adduct of hexamethylene diisocyanate in PCS preparations.

INTRODUCTION

Polyurethanes with terminal $-NHCOSO_3^-$ salt groups, *i.e.*, polycarbamoyl sulphonates (PCSs), are used in the textile industry, mainly to shrink-resist wool[1,2]. For mechanistic studies on these PCS shrink-resist treatments, methods were needed to follow the complex chemical changes occurring during the manufacture and application of PCSs, but the only published method was the estimation of the carbamoyl sulphonate group content by titration[1]. This paper describes chromatographic techniques for the more detailed analysis of PCSs and for following changes in molecular weight distribution during the preparation and curing of PCSs.

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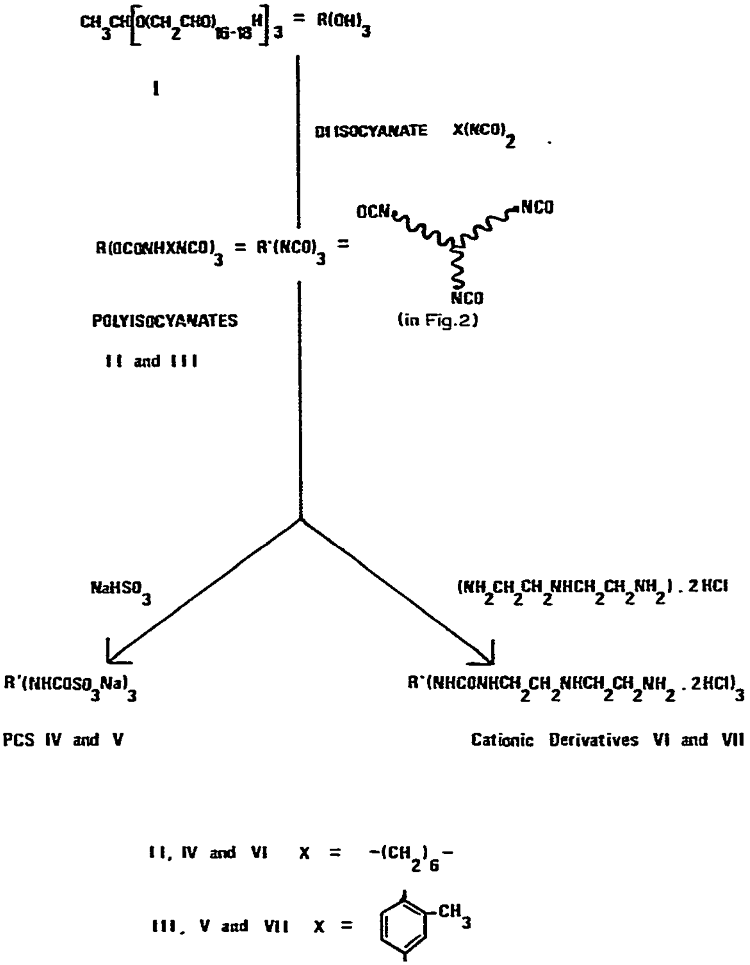

Fig. 1. Preparation of polycarbamoyl sulphonates.

The PCSs used industrially on wool and for this study were prepared (see Fig. 1) from poly(propylene oxide) polyols via isocyanate-terminated prepolymers (polyisocyanates). Such polyols and polyisocyanates are widely used to make polyurethane surface coatings and elastomers[3], but have been studied by chromatographic techniques only to a limited extent[4–7]. Such polyols will have a narrow, Poisson-type molecular weight distribution, but reactions occurring subsequently (Fig. 2) result in a complex polymodal distribution for the polyisocyanates and PCSs derived from these polyols. Attention has been directed at gel permeation chromatographic (GPC) methods to determine the molecular weight distribution of PCSs and polyisocyanates since it is usually not possible to calculate these distributions, and other molecular weight techniques only give averages.

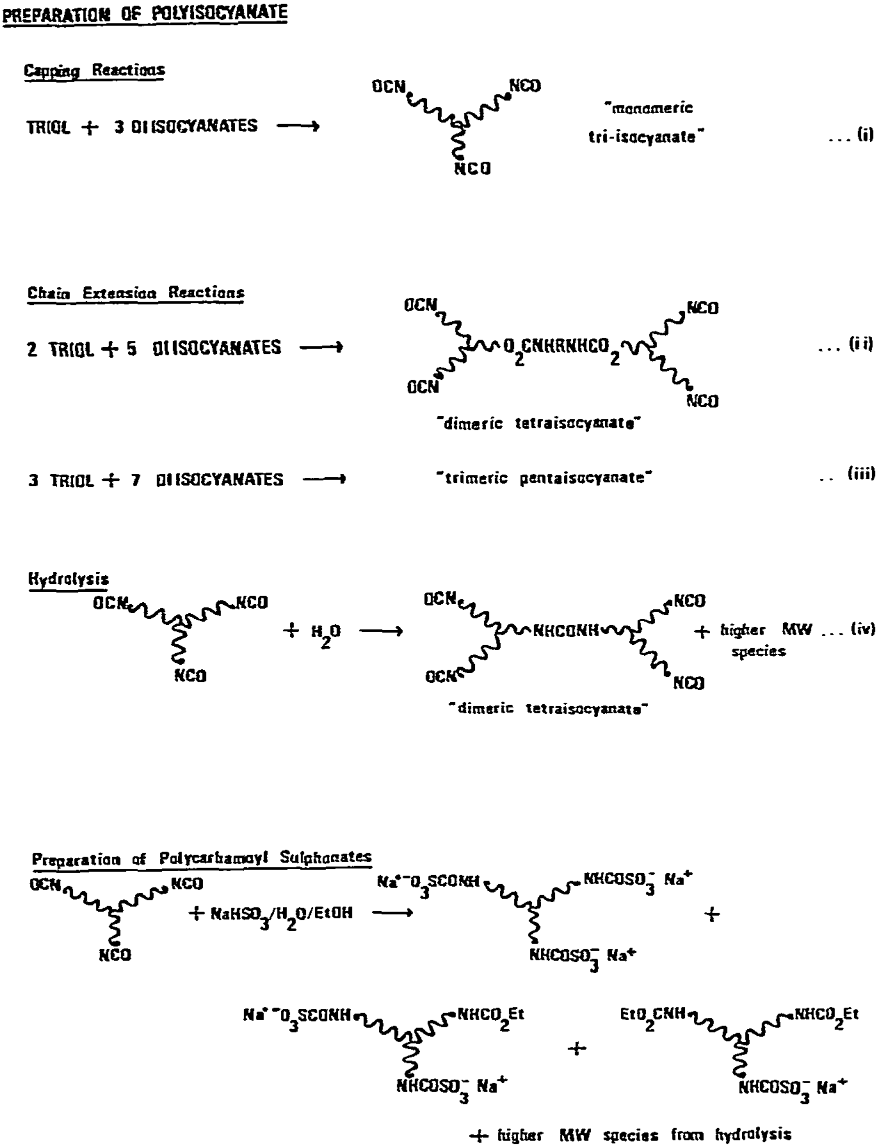

Fig. 2. Various reactions in PCS preparation from a triol + diisocyanates. Et = Ethyl. MW = molecular weight.

EXPERIMENTAL

Chromatography

A Varian 4100 syringe pumping system with a Rheodyne injector with a 100- or 500-μl loop was used with a Varian refractive index detector, or a Varian Varichrom variable-wavelength detector set at 230 nm.

The following columns were used: (A) Shodex A803 (Showa Denko, Tokyo, Japan), polystyrene gel (run with tetrahydrofuran solvent at 30°C and 1.0 ml/min flow-rate). This column was calibrated with poly(propylene oxide) glycol standards (Waters Assoc., Milford, MA, U.S.A.). (B) TSK-3000SW (Toyo Soda, Tokyo, Japan) a surface modified silica (run with aqueous solvents at 22°C and 1.3 ml/min flow-rate). This column was calibrated with dextran standards (Pharmacia, Uppsala, Sweden) and sucrose. (C) LiChrosorb RP-8 (Merck, Darmstadt, G.F.R.), a reversed-phase support packed in this laboratory into a 250 × 4.6 mm I.D. column (run at 22°C and 1.0 ml/min flow-rate).

Materials

Methyltrioctylammonium chloride (Aliquat 336; was technical grade; all other chemicals used were analytical grade. Tetrahydrofuran (THF) was freshly redistilled (AR grade; BDH, Poole, Great Britain), and if necessary dried by distillation from calcium hydride.

Polymers

The synthesis and structure of the various polymers are summarized in Fig. 1.

Polyisocyanate II

Polyisocyanate II was prepared by heating the polyol (I) (Desmophen 3400; Bayer, Leverkusen, G.F.R.) (see Fig. 1 for structure) with an equimolar portion of hexamethylene diisocyanate at 100°C under dry nitrogen for 5 h. The isocyanate content, determined by the addition of excess di-*n*-butylamine and back titration with dilute hydrochloric acid, was 3.99%.

Polyisocyanate III

Polyisocyanate III was prepared by heating Desmophen 3400 with an equimolar portion of 2,4-tolylene diisocyanate for 2 h at 70°C under dry nitrogen. The isocyanate content was 3.74%.

Polycarbamoyl sulphonates[1]

Polyisocyanate II (20 g) in ethyl acetate (5 ml) was reacted with sodium bisulphite (1.1 equivalents) in a mixture of water (60 ml) and ethanol (140 ml) to give a solution of PCS-IV.

A 20% solution of PCS-V was prepared by reaction of polyisocyanate III with sodium metabisulphite (1.1 equivalent) and triethylamine (0.2 equivalent) in isopropanol–water (60:40). After 10 min the reaction mixture was adjusted to pH 4 with dilute sulphuric acid.

Cationic derivatives VI and VII[8]

A solution of diethylenetriamine (1.1 equivalents) in ethanol (250 ml) was adjusted to pH 6 by the addition of 2 *M* hydrochloric acid (≈50 ml) and then stirred while a solution of the polyisocyanate (40 g) in dioxan (40 ml) was added. After 10 min the pH of the solution was adjusted to 4.

GPC of PCSs Aliquat 336 method. A 50% aqueous solution of PCS (3 drops) was mixed with methyltrioctyl–ammonium chloride (Aliquat 336, 1 drop), THF (2 ml) was added and the solution was either filtered or the solids (presumably sodium bromide) were allowed to settle before injection of a sample of the solution into the chromatograph. It was not necessary to remove the water from the PCS sample since the water peak is well resolved from the polymeric material in the GPC.

1-(2-Pyridyl)piperazine derivatization method. A solution of PCS (1 g of 50% solution diluted to 10 ml) was mixed with a solution of 1-(2-pyridyl)piperazine (0.1 g in 5 ml) and the mixture was kept at 50°C for 10 min, during which time the derivative precipitated. The solution was decanted off and the precipitate was washed with water (15 ml). The product was then dissolved in THF ($\approx$ 0.05 g in 2 ml) and chromatographed.

RESULTS AND DISCUSSION

GPC of neutral polymers

The neutral polyol I and polyisocyanates II and III were chromatographed on a polystyrene gel column in THF (Fig. 3). Even though polyisocyanates react readily with moisture, it was not necessary to dry the THF or to convert them to unreactive derivatives as previous workers have done (*e.g.* by reaction with methanol[4,6]). Changes were, however, observed when polyisocyanate II was exposed to atmosphere moisture for long periods (Fig. 3e).

Molecular weights were assigned to the polymer peaks by direct calibration against commercial poly(propylene oxide) molecular weight standards. There may be slight errors in this approach since the polymers studied were branched and contained up to 10% (w/w) of end groups. However, the errors were probably no greater than those in the molecular weights from vapour phase osmometry (Table I). Polyol I has a slightly higher molecular weight by osmometry than expected, and this may be due to association of solvent with the terminal hydroxyl groups[9].

The polyol I had a single narrow GPC peak, but the derived polyisocyanates showed several peaks in GPC with a much wider spread of molecular weights (Fig. 3). Fig. 2 summarizes the reactions which give rise to this polymodal molecular weight distribution. In the preparation of polyisocyanates, the main reaction (i) gives "monomeric" (*i.e.* relative to polyol) species. Chain extension reactions (ii) and (iii) form higher-molecular-weight "dimeric", "trimeric" etc. species, but consume less diisocyanate so there is also a low-molecular-weight peak of unreacted diisocyanate.

Polyisocyanate II (derived from hexamethylene diisocyanate) showed from "monomer" up to "tetramer" peaks and a higher-molecular-weight tail. In contrast, polyisocyanate III (from tolylene diisocyanate) showed only peaks up to trimer. This narrower molecular weight distribution is expected because the unequal reactivity of the two isocyanate groups in 2,4-tolylene diisocyanate favours the capping reaction (i) over chain extension reactions (ii) and (iii) (Fig. 2).

Aqueous GPC of PCSs

Polystyrene gel GPC columns are limited to organic eluents, but recently columns of surface-modified silica gel have been developed for aqueous GPC[10,11]. Only one column of this type (TSK-3000SW; Toyo Soda) has been examined, as this appeared to offer the best resolution in the molecular weight range of interest (2–20,000). PCS-IV on this column tailed badly when eluted with water, but this tailing was suppressed by adding to the eluent either salts or methanol together with smaller amounts of salts. When this was done the GPC of PCS-IV (Fig. 4) showed several

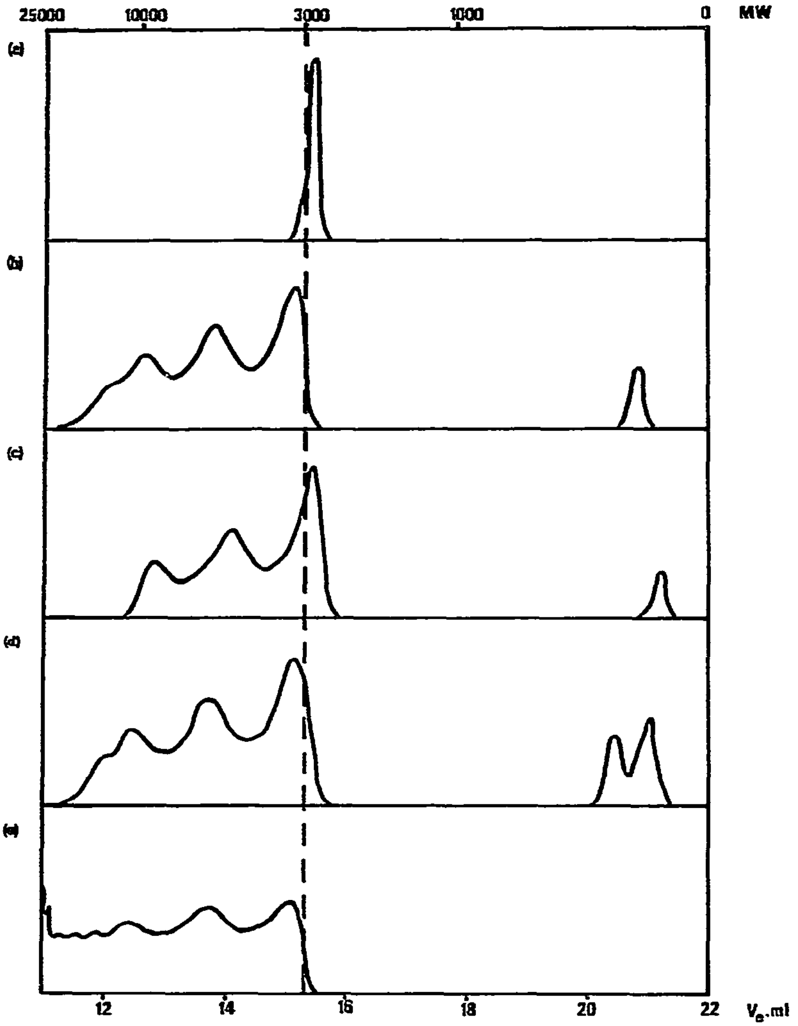

Fig. 3. GPC of (a) polyol I, (b) the derived polyisocyanate II, (c) polyisocyanate III, (d) dibutylamine derivative of II, and (e) product of II + atmospheric moisture for 24 h. R^+ 20°C. Eluent: THF; detector: refractive index; column: polystyrene gel. V_e = Elution volume.

peaks, but the number and position of these was very dependent on the pH and ionic strength. Generally the apparent molecular weight of the peaks decreased when the eluent was made more acidic and also when the ionic strength was raised; similar shifts have been noted in the aqueous GPC of other anionic polymers[10]. As a consequence of these peak shifts, it was not possible to compare the molecular weight distribution of PCS and the parent polyisocyanates. However, this aqueous GPC system may be useful for the analysis of the bisulphite adduct of hexamethylene diisocyanate (VIII) in PCS-IV. Under certain conditions (Fig. 4a) the peak for VIII was well separated from the other solvent, salt and polymeric peaks.

$$Na^+\ {}^-O_3SCONH(CH_2)_6NHCOSO_3^-\ Na^+ \qquad \text{(VIII)}$$

TABLE I

VAPOUR PHASE OSMOMETRY AND INTRINSIC VISCOSITY DATA OF POLY(PROPYLENE OXIDES) (PPOs), POLYISOCYANATES AND DERIVATIVES

Polymer	*Solvent*	*Stated mol. wt.*	$\bar{M}_n$*	$[\eta]$
PPO standard	THF	800		0.03
PPO standard	THF	1220		0.04
PPO standard	THF	2000		0.063
PPO standard	THF	4000		0.062
Polyol-I	THF	3000	3300	0.067
Polyisocyanate II			3200	0.19
PCS-IV	THF + 0.5% H_2O		12000**	0.16
PCS-IV	THF + 1% H_2O		3200	0.16
PCS-IV	THF + 2% H_2O		3300	***
PCS-IV–LiCl	THF		4300	0.14
PCS-IV–Aliquat 336	THF		2300	0.20

* From vapour phase osmometry.
** Fell to 6000 after 90 min.
*** Not measured.

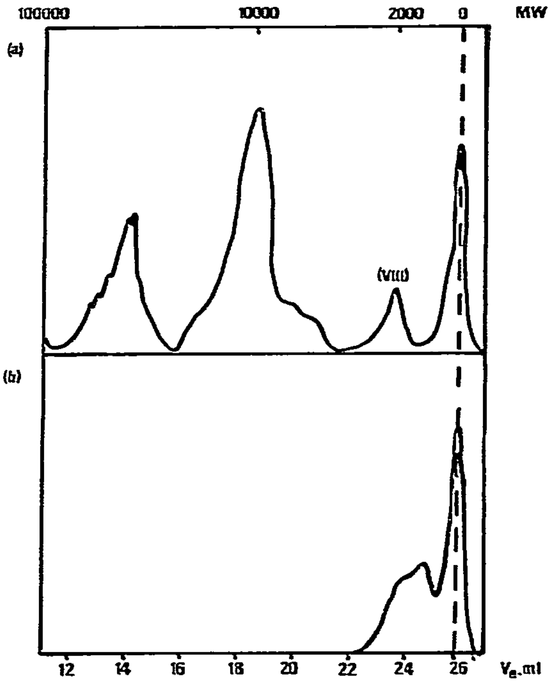

Fig. 4. GPC of PCS-IV. Eluent: (a) 0.01 *M* $NaNO_3$ in water at pH 7; (b) 0.01–0.1 *M* $NaNO_3$ in water at pH 3; column: TSK-3000SW; detector: refractive index.

GPC of PCSs on polystyrene gel columns

A method to chromatograph PCSs on polystyrene gel columns was needed for direct comparisons of the molecular weight distributions of PCSs with those of the polyol and polyisocyanates from which the PCSs were derived. The insolubility of PCSs in organic solvents prevented them from being chromatographed on polystyrene gel columns. This problem could be overcome by conversion of the PCSs into neutral THF-soluble derivatives, but to assign molecular weights there should be no change in the molecular distribution during the preparation of the derivative, *e.g.* by fractionation or polyfunctional side reactions such as the hydrolysis of isocyanates or carbamoyl sulphonates.

PCSs were converted into neutral derivatives by reaction with di-*n*-butylamine. The chromatograms (Fig. 3) of the di-*n*-butylureas from both PCS-IV and polyisocyanate II were very similar to that of polyisocyanate II. This suggests that the molecular weight distribution did not change significantly when II was converted into IV, and when II or IV was reacted with di-*n*-butylamine. To support this conclusion, alternative GPC methods based on increasing the solubility of PCSs in THF were examined.

Chromatograms of PCS-IV and -V on polystyrene gel columns could be obtained by adding 0.5% or more water to the THF eluent. With 0.5% water there was a broad peak which tailed to high molecular weights. As the water concentration was increased, tailing was suppressed and the peaks were shifted to lower apparent molec-

TABLE II

SOLUBILITY AND GPC OF PCS CATION COMPLEXES

Sol. = Soluble; Insol. = insoluble; Sl. sol. = slightly soluble.

*Cation**	*Solubility*		*GPC****	
	*THF***	*0.5% Water in THF*	*Mol. wt.*	*Comments*
$C_{16}H_{33}N^+(CH_3)_3$	Insol.	Sol.	8000–4000	Moderate resolution
$(C_8H_{17})_3N^+CH_3$ (Aliquat 336)	Sol.	Sol.	10,000; 6800; 3500	Good resolution
$(C_4H_9)_4\ N^+$	Insol.	Sol.	6000; 3000	Poor resolution
$(C_2H_5)_4\ N^+$	Insol.	Insol.	§	
$C_6H_5CH_2N^+(C_4H_9)_3$	§	Sol.	5500; 2500	Poor resolution
$N^+C_{16}H_{33}$	Insol.	Sol.	5500; 2500	Poor resolution tailing peaks
Na^+	Insol.	Sl. sol.	20,000–3500	Poor resolution §§
Na^+ (18-crown-6)	Insol.	Sol.	15,000–3500	Poor resolution §§
Li^+	Insol.	Sol	9000; 6000; 3500	Moderate resolution §§

* Introduced by mixing 1.1 equivalents of the required reagent wiuh PCS sodium salt.

** Dried over calcium hydride.

*** In 0.5% H_2O in THF unless otherwise stated. Molecular weights should be 3900, 7000, 11,000, etc. based on the structures of PCS-IV shown in Figs. 1 and 2 and based on the GPC of the Polyol-I.

§ Not tested.

§§ See Fig. 5.

ular weights. The chromatogram of PCS-IV with 2% water in THF was very similar to that of the parent polyisocyanate II in dry THF. Since the manufacturer of the polystyrene gel columns stated that water caused the column performance to deteriorate, an examination was made of other methods known to increase the solubility of salts in organic solvents, *e.g.*, the addition of crown ethers or the replacement of sodium by lithium or quaternary ammonium ions. Experiments of this type are summarised in Table II and selected chromatograms shown in Fig. 5. An increase in the THF solubility was generally accompanied by a shift of the PCS peaks to lower apparent molecular weights. These changes appear to be consistent with different extents of aggregation of the PCS molecules and separation by the GPC column of these aggregates. Examples have been reported of the aggregation in organic solvents of polymers with terminal $-SO_3^-$ groups[12,13] and of aggregation effects in GPC[14,15]. The viscosity and the molecular weight from vapour phase osmometry (Table I) also changed when the cation or water content changed, but there was no consistent pattern in these results to confirm the aggregation hypothesis. The results in Table I clearly show the problems associated with the use of conventional molecular weight techniques on PCSs.

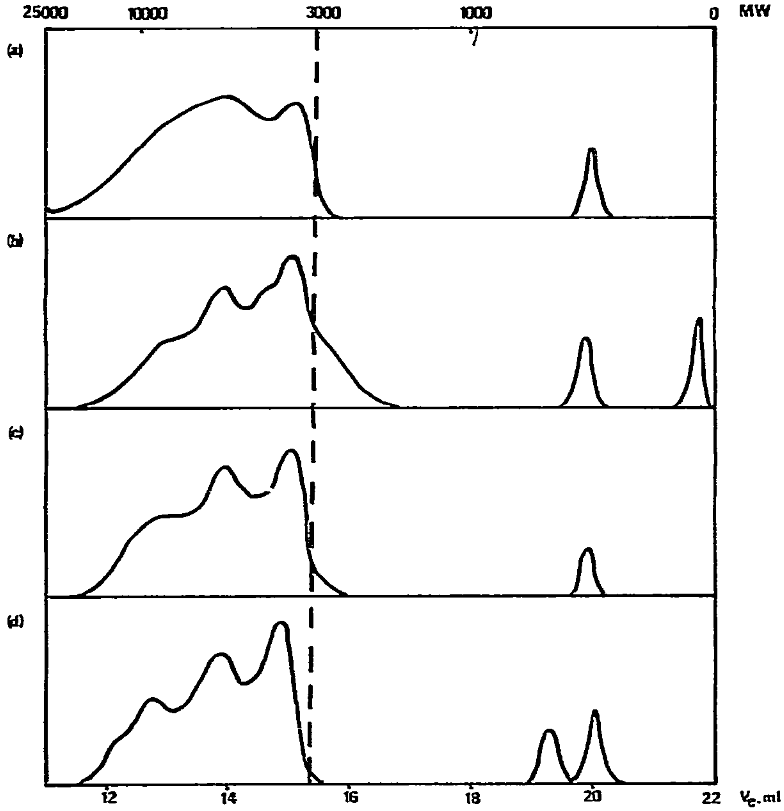

Fig. 5. GPC of (a) PCS-IV; (b) PCS-IV 18-crown-6 (1.1:1 equivalents per carbamoyl sulphate); (c) PCS-IV + lithium chloride (1.1:1); (d) PCS-IV + Aliquat 336 (1.1:1). Eluent: 0.5% water in THF; detector: refractive index; column: polystyrene gel.

The PCS–Aliquat 336 complex salt was preferred for GPC for the following reasons: (i) it was soluble in dry THF (unlike the lithium and cetyltrimethylammonium salts); (ii) it had a GPC behaviour very similar to that of the parent polyisocyanate (whereas the 18-crown-6 ether showed a higher apparent molecular weight); (iii) it did not adsorb on the column (as did quaternary ammonium salts with aromatic groups); and (iv) it was not concentration dependent (like the lithium and sodium salts).

In Fig. 6 the chromatograms are shown for different proportions of Aliquat 336 and PCS-IV. Increasing the proportion of Aliquat 336 up to about 1.1 equivalents increased the solubility in THF (as shown by increased peak intensities) and decreased the intensity of the high-molecular-weight peaks whilst increasing that of the lower-molecular-weight peaks. Adding more than 1.1 equivalents caused no further changes in the GPC behaviour.

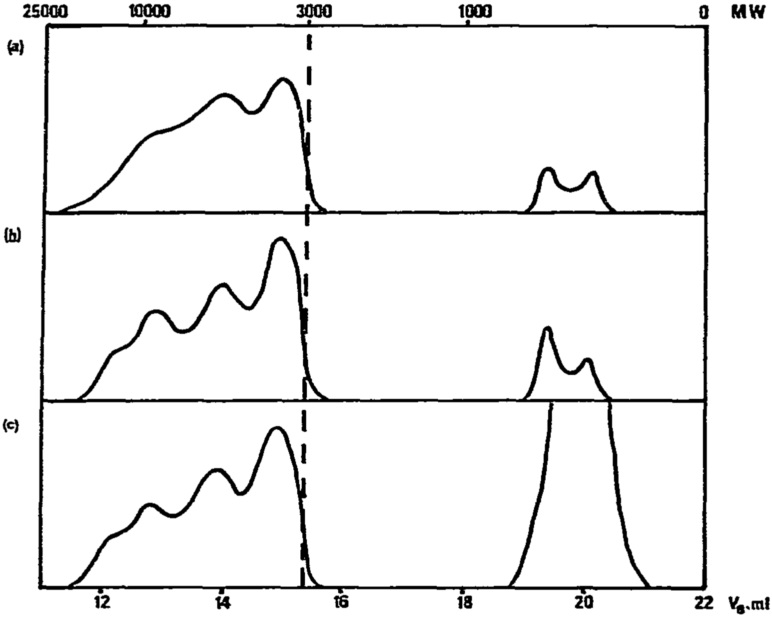

Fig. 6. The effect of changes in the ratio of equivalents of Aliquat 336 to PCS-IV on the GPC. (a) Ratio = 0.5; (b) ratio = 1.1; (c) ratio = 10. Eluent: THF; detector: refractive index; column: polystyrene gel.

In the PCS solubilizing methods developed here, it should be noted that the quaternary ammonium salt is only added to the sample and not to the running solvent, and that only just over one equivalent is used. Thus the method is different from other ion-pairing techniques[16] in chromatography which involve the addition of surfactants to the running solvent.

The scope of our technique has been investigated with a range of other polyelectrolytes and surfactants of opposite charge. In many cases THF-soluble complexes readily formed but in most cases (*e.g.* polystyrene sulphonic acid, polyvinylimidazolium salts, polydiallyldimethylammonium chloride polymers) GPC was unsatisfactory due to adsorption. The method appears to be limited to polymers with a relatively small number of ionic groups, and is most suitable for those with ionic groups at chain ends.

Comparison of GPC methods for PCSs

The Aliquat 336 method has been used to examine fractions from aqueous GPC of PCS-IV on the TSK-3000SW column. This indicated that both columns were separating on the same size-exclusion basis, *e.g.*, material from the "monomeric" peak of the aqueous chromatography showed essentially only "monomeric" material after GPC of the Aliquat 336 salt on the polystyrene gel column. The main advantage of the Aliquat 336 method is that the molecular weights assigned to the PCS peaks were very close to the calculated values and it is much more rapid than derivatization of PCSs with di-*n*-butylamine.

Cationic polyurethane derivatives

The GPC methods developed for PCSs have been used to investigate the cationic polyurethanes VI and VII which are derived (see Fig. 1) from polyisocyanates II and III and have been reported to shrink-resist wool[8]. These cationic polymers could not be chromatographed in aqueous solutions on the TSK-3000SW columns, due to excessive adsorption and a much greater dependence of the peak elution volumes on the ionic strength. However, they could be chromatographed in dry THF on polystyrene gel columns (Fig. 7) by forming a complex salt with an anionic surfactant. The best results were obtained with sodium lauryl sulphate.

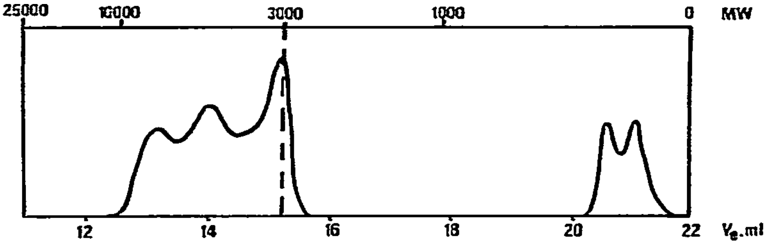

Fig. 7. GPC of the cationic polyurethane derivative (VI)–dodecylsulphate complex. Eluent: THF; detector: refractive index; column: polystyrene gel.

Reversed-phase chromatography of PCSs

Reversed-phase chromatography was examined as a means of analysing the low-molecular-weight species in PCSs which elute in GPC in a single peak at the total permeation limit. PCS-IV when chromatographed on LiChrosorb RP-8, eluting with water–methanol mixtures, gave peaks due to ethanol, ethyl acetate, the bisulphite adduct of hexamethylene diisocyanate, and some minor unidentified peaks (Fig. 8). In experiments in which the peaks from reversed-phase chromatography were collected and rechromatographed by the two GPC systems, it was established that the polymeric material in PCS-IV and -V was retained on the column. The PCS was not displaced from the column by adding sodium sulphate or sodium lauryl sulphate, although addition of tetrahydrofuran eluted the PCSs at the solvent front.

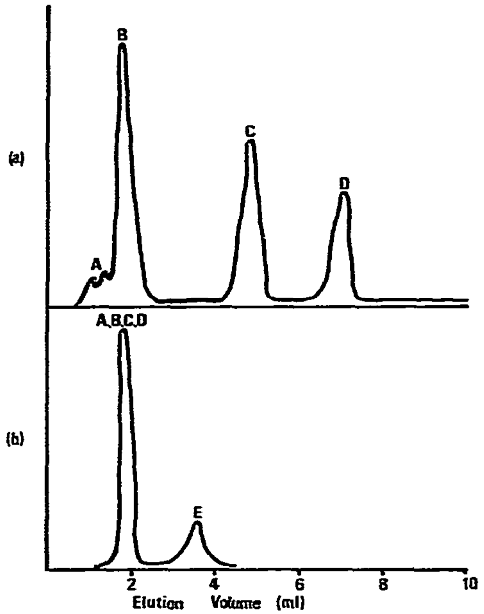

Fig. 8. Reversed-phase chromatogram of PCS-IV in (a) methanol–water (10:90) and (b) methanol–water (80:20). A = unidentified; B = VIII; C = ethanol; D = isopropanol; E = ethyl acetate. Detector: refractive index.

Concentration of carbamoyl sulphonates in GPC peaks from PCSs

The number of end groups per molecule in the various GPC peaks of polyisocyanates and PCSs will be different. For the example in Fig. 2, if there are no side reactions, the monomeric, dimeric and trimeric peaks will have 3, 4 and 5 end groups, respectively. Thus a chromatogram using a detector proportional to the polymer concentration (*e.g.* refractive index or ultraviolet (UV) absorption at 230 nm) will be quite different to one using a detecting system related to the number of end groups (*i.e.* isocyanates or carbamoyl sulphonates). A detection system of the latter type has been devised in order to investigate the side reactions (see Fig. 2) in PCS manufacture.

It is possible to collect fractions of the GPC eluent and analyse for end groups. This was carried out with PCS-IV on the TSK-3000SW column since this had a greater capacity compared with the polystyrene gel column, but due to the insensitivity of the analytical method[17] there were large errors, and fractions from a number of replicate chromatograms had to be pooled. The conversion of the carbamoyl sulphonate groups to derivatives with a strong UV absorption was then examined. Substitution of Aliquat 336 by UV-absorbing quaternary ammonium salts (*e.g.*, cetylpyridinium chloride) was unsatisfactory, as the corresponding PCS salts adsorbed onto polystyrene gel columns. 1-(2-Pyridyl)piperazine reagent has been used to analyse diisocyanates[18] by forming a UV-absorbing derivative. This reagent is water-soluble and when added to aqueous PCS solutions rapidly formed an insoluble product with an ultraviolet peak at 300 nm ($\varepsilon = 3300 \text{ l mol}^{-1} \text{ cm}^{-1}$). Chromatograms of the 1-(2-pyridyl)piperazine derivative of PCS-IV are shown in Fig. 9. A comparison of the UV response at 300 nm with that from the refractive index detector gave the expected proportions of carbamoyl sulphonates in the various peaks. This derivatization method also provides a sensitive method for estimating the bisulphite adduct of hexamethylene diisocyanate (VIII) in PCS-IV. The peak for the derivative is sharp and well resolved. This reagent can be used in non-aqueous solutions to form derivatives from polyisocyanates II and III, thus providing a means of investigating the number of isocyanate end groups in the GPC peaks in polyisocyanates.

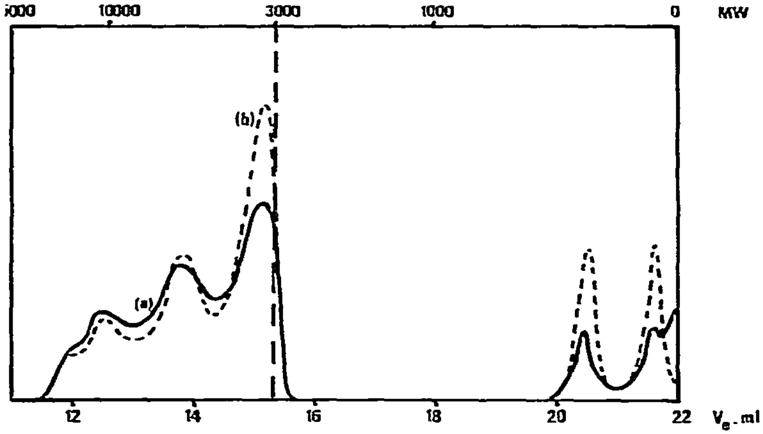

Fig. 9. GPC of PCS-IV, 1-(2-pyridyl)piperazine derivative. Eluent: THF; detector: (a) refractive index, (b) UV (300 nm) absorption; column: polystyrene gel.

CONCLUSIONS

Methods have been developed for the analysis of PCSs of the type used to shrink-resist wool, using chromatographic techniques. Several GPC methods can be used to investigate the molecular weight distribution of PCSs. All show the expected complex polymodal molecular weight distribution. The best method involves mixing the PCSs with methyltrioctylammonium chloride and chromatography of the complex salt formed in THF on polystyrene gel columns. This method is rapid and avoids the problems of possible side reactions associated with the conversion of PCSs into neutral derivatives, and the effects of pH and ionic strength on the peak positions found in the aqueous GPC of PCSs or surface-modified silica columns. Even though in some cases better resolution of the polymeric peaks was observed in aqueous GPC, there was much greater error in the apparent molecular weights. The GPC data have so far only been used in a qualitative manner, but it should also be possible to calculate molecular weight averages and the proportions of "monomeric" etc. species.

This technique of solubilizing ionic polymers for GPC by formation of salt with a long chain organic ion of opposite charge was also used for some related cationic polyurethanes but was not suitable for other polyelectrolytes. These methods appear to be restricted to polymers with a small number of charged groups, *e.g.*, at chain ends.

A method to estimate the number of carbamoyl sulphonate groups in the GPC peaks of PCSs was devised. This involved reaction of PCS with excess [1-(2-pyridyl)-

piperazine] and comparison of the GPC (in THF on polystyrene gel) of the UV response at 300 nm with that from a refractive index detector.

Several techniques can be used to analyse low-molecular-weight species (*e.g.*, solvents and diisocyanate bisulphite adducts) in PCS preparations. GPC on polystyrene gels did not resolve species below molecular weight 300, but it was possible, by suitable choice of eluent in the aqueous GPC of PCS-IV, to separate the bisulphite adduct of hexamethylene diisocyanate (VIII) as a distinct peak. Reversed-phase chromatographic techniques could also be used to estimate VIII, and also solvent (*e.g.*, ethanol, isopropanol or ethyl acetate) residues. The most sensitive technique to analyse for VIII was derivatization with 1-(2-pyridyl)piperazine and GPC on polystyrene gel.

To summarize, it is possible with one column and eluent (polystyrene gel and THF)

(i) to follow changes in the molecular weight distribution in the sequence poly(propylene oxide) polyols → polyisocyanates → PCS;

(ii) to estimate the proportion of terminal carbamoyl sulphonate groups in the PCS peaks; and

(iii) to estimate the amount of hexamethylene diisocyanate bisulphite adduct.

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