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Note

Separation of isocyanate prepolymer components as their urea derivatives by reversed-phase high-performance liquid chromatography

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High-molecular-weight, polyfunctional isocyanates are extensively used in industry, primarily because they will react with polyhydroxy compounds to form polyurethane products, such as flexible and rigid foams, solid elastomers, surface coatings, fibres and adhesives. Although most manufacturers of polyfunctional isocyanates (or, as they are generally called, isocyanate prepolymers) supply an idealised formula for each of their compounds, the majority of these commercial products also contain other high-molecular-weight polyisocyanates and, in most cases, residual amounts of the parent monomer.

Several papers have reported the high-performance liquid chromatographic (HPLC) separation of residual isocyanate monomers in commercial isocyanate prepolymers[1–5]. However, the separation of the various polyfunctional isocyanate-containing components of a range of commercial prepolymers or oligomers, based on their conversion to the corresponding ureas followed by high-performance thin-layer chromatography, has only been reported by Ellwood *et al.*[6]. This paper describes a method using a reversed-phase HPLC procedure with ODS-Hypersil for the resolution of several commercial isocyanate prepolymers after their conversion to stable urea derivatives by reaction with 1-(2-pyridyl)piperazine.

EXPERIMENTAL

Chromatographic apparatus

The liquid chromatograph consisted of an Altex Model 110A constant-flow reciprocating diaphragm pump, a Rheodyne Model 7120 syringe-loading sample injector with a 20-μl loop and a Pye-Unicam LC-UV detector set at 254 nm. The column used was a 25 cm × 4.6 mm I.D. length of Apollo stainless-steel tubing, slurry-packed at 6000 p.s.i. with ODS-Hypersil (5 μm diameter mean particle size, Shandon Southern Products, Runcorn, U.K.). The mobile phase was de-aerated with helium and pumped at ambient temperature through the column at a flow-rate of 2.0 ml/min.

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Mobile phase

The mobile phase consisted of acetonitrile in 0.1 *M* aqueous ammonium acetate solution (1:1). The pH of the ammonium acetate solution was adjusted to 6.2 by addition of acetic acid.

Isocyanates

The following isocyanates were used: 1,6-hexamethylene diisocyanate (HMDI) (Desmodur H; Bayer, Leverkusen, F.R.G.); HMDI-based prepolymer (Desmodur N; Bayer); 4,4′-methylene bisphenyl isocyanate (MDI), (ICI, Macclesfield, U.K.); crude MDI (Desmodur VL; Bayer); 2,4-toluene diisocyanate (2,4-TDI), (Fluorochem, Glossop, U.K.); 2,6-toluene diisocyanate (2,6-TDI), (ICI, Blackley, Manchester, U.K.); TDI-based prepolymers (Desmodur L and IL; Bayer); HMDI/TDI-based prepolymer (Desmodur HL; Bayer).

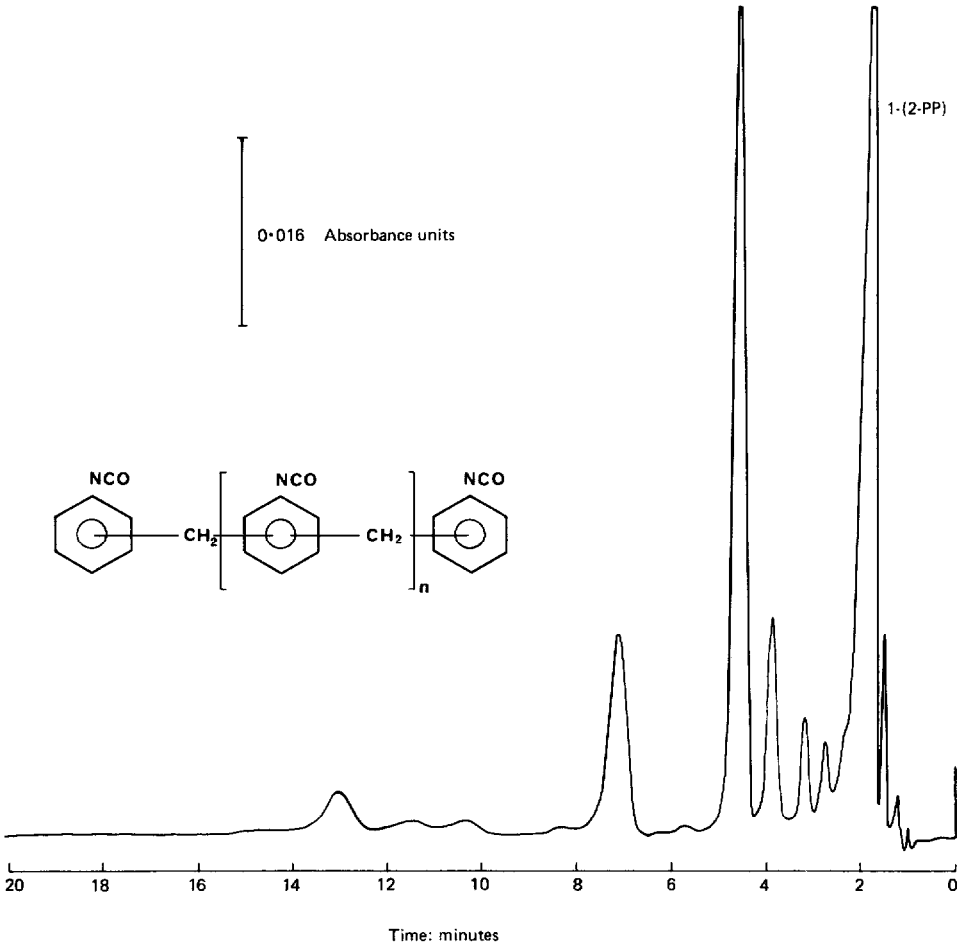

Fig. 1. Chromatogram of crude MDI urea derivatives together with excess reagent. Conditions: column, 250 × 4.6 mm I.D. ODS-Hypersil (5 μm); mobile phase, acetonitrile–0.1 *M* aqueous ammonium acetate (1:1), the water phase adjusted to pH 6.2 with acetic acid; temperature, ambient; flow-rate, 2.0 ml/min; sample volume, 20 μl; detection, UV at 254 nm and 0.08 a.u.f.s.

Standard urea derivatives

A freshly prepared solution of the relevant isocyanate monomer or prepolymer (0.8 mmol) in 3 ml of a dry, water-miscible solvent (dimethyl sulphoxide, dioxane, etc.) was added to a stirred solution of excess (1.8 to 10.0 mmol, depending on the –NCO functionality of the prepolymer) 1-(2-pyridyl)piperazine (Aldrich, Gillingham, U.K.) in the same solvent (3 ml). The commercially supplied reagent contains up to 5% of 1,4-(2,2'-dipyridyl)piperazine. The pure reagent was prepared by vacuum distillation from the commercial material; the boiling point of 1-(2-pyridyl) piperazine is 114°C at 3 mmHg. After stirring for approximately 30 min at 60°C, the reaction mixture was flooded with 200 ml of distilled water. The white precipitate which formed was filtered off and washed with copious amounts of distilled water. In order to maintain the original percentage composition of the isocyanate components of the prepolymer, the isocyanate prepolymer urea derivatives so prepared were not recrystallised.

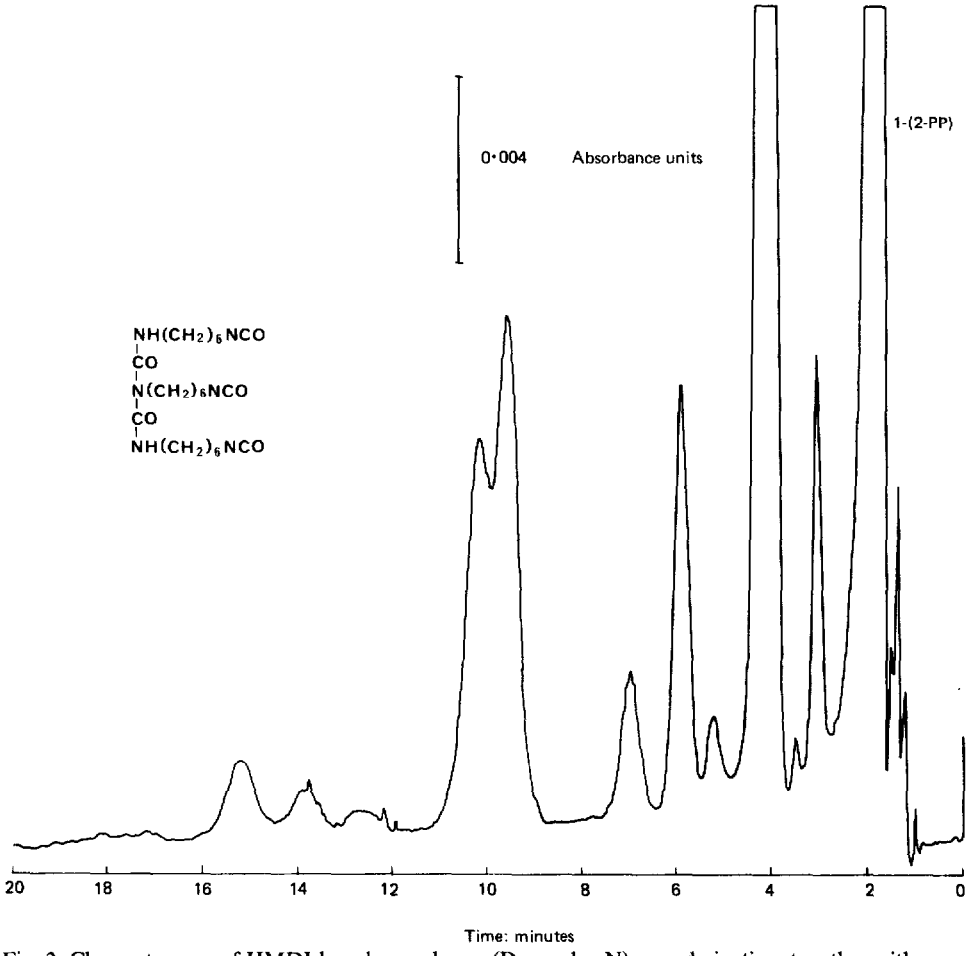

Fig. 2. Chromatogram of HMDI-based prepolymer (Desmodur N) urea derivatives together with excess reagent. Conditions as in Fig. 1, except: sensitivity, 0.02 a.u.f.s.

Standard solutions

Standard solutions containing 50 μl/ml of each of the prepolymer urea derivative samples were prepared.

The idealised formulae of the isocyanate prepolymers studied were assumed[7] to be $C_{23}H_{38}N_6O_5$ (Desmodur N), $C_{33}H_{32}N_6O_9$ (Desmodur L), $C_{45}H_{30}N_{10}O_{10}$ (Desmodur IL), $C_{43}H_{42}N_{10}O_{10}$ (Desmodur HL) and $C_{23}H_{15}N_3O_3$ (crude MDI). Aliquots (20 μl) of the standard solutions were injected into the liquid chromatograph.

RESULTS AND DISCUSSION

Previous work[8] has shown that ODS-Hypersil is the most suitable reversed-phase column packing for the separation of the urea derivatives of isocyanate mono-

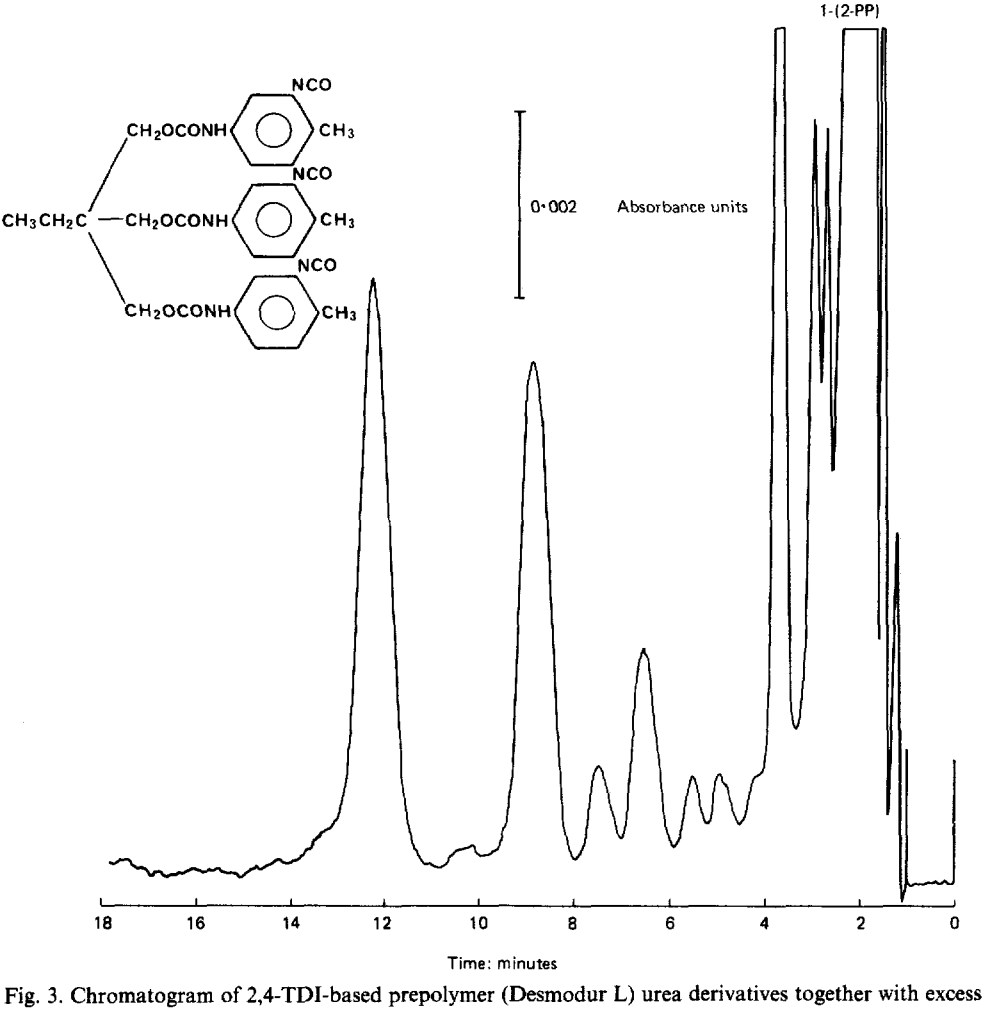

Fig. 3. Chromatogram of 2,4-TDI-based prepolymer (Desmodur L) urea derivatives together with excess reagent. Conditions as in Fig. 1, except: sensitivity, 0.01 a.u.f.s.

mers and consequently this was used in the present work. Using an acetonitrile–buffered ammonium acetate mobile phase, excess 1-(2-pyridyl)piperazine reagent is eluted first. Figs. 1–5 show chromatograms of the urea derivatives of crude MDI, desmodur N, L, IL and HL, respectively; idealised formulae of the parent prepolymers are also shown. The separation of all the main components of a commercial prepolymer enables the quantification of many airborne prepolymer concentrations to be achieved by sampling the test atmosphere through a $2 \cdot 10^{-4}$ *M* solution of 1-(2-pyridyl)piperazine as previously described for isocyanate monomers[6]. However, such a procedure will be viable only for industrial polyurethane-formation processes which have relatively long curing times such as the surface coating operations for which Desmodur L and N are used. Atmospheric samples obtained during fast curing processes, such as the spraying of roof surfaces with crude MDI-based polyurethane foam, will contain additional isocyanate species, formed by the partial reaction of the prepolymer components with polyol. In these cases, the standard prepolymer urea derivative peaks will not correspond with the sample, and consequently the determination of total airborne prepolymer concentration will not be viable.

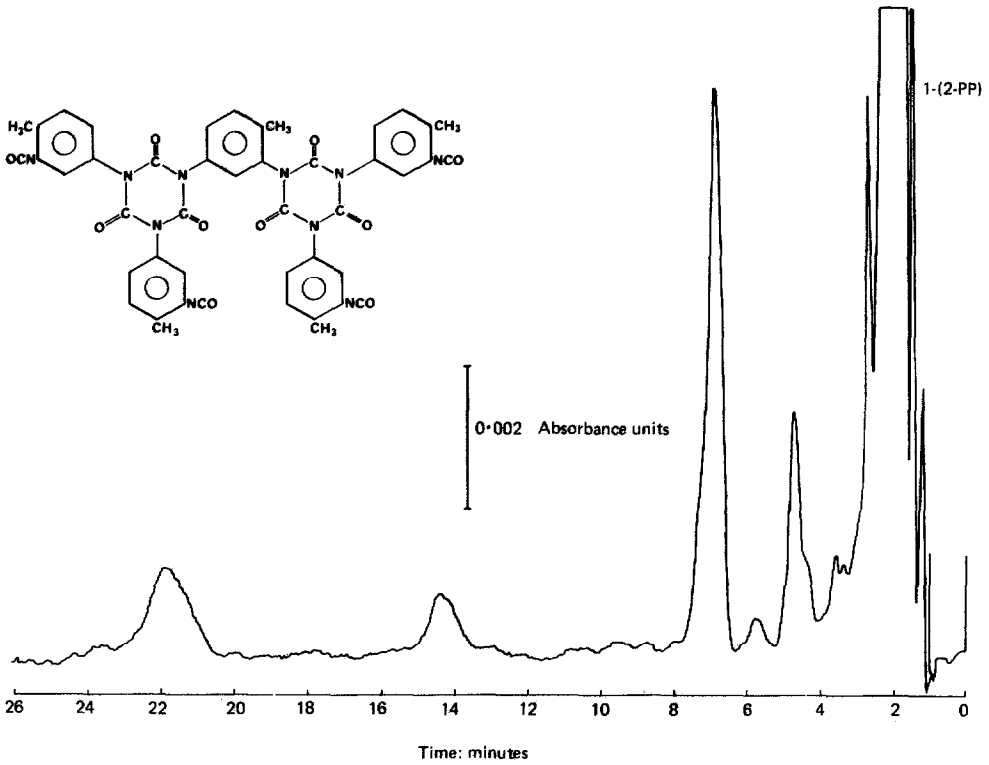

Fig. 4. Chromatogram of 2,4-TDI-based prepolymer (Desmodur IL) urea derivatives together with excess reagent. Conditions as in Fig. 1, except: sensitivity, 0.01 a.u.f.s.

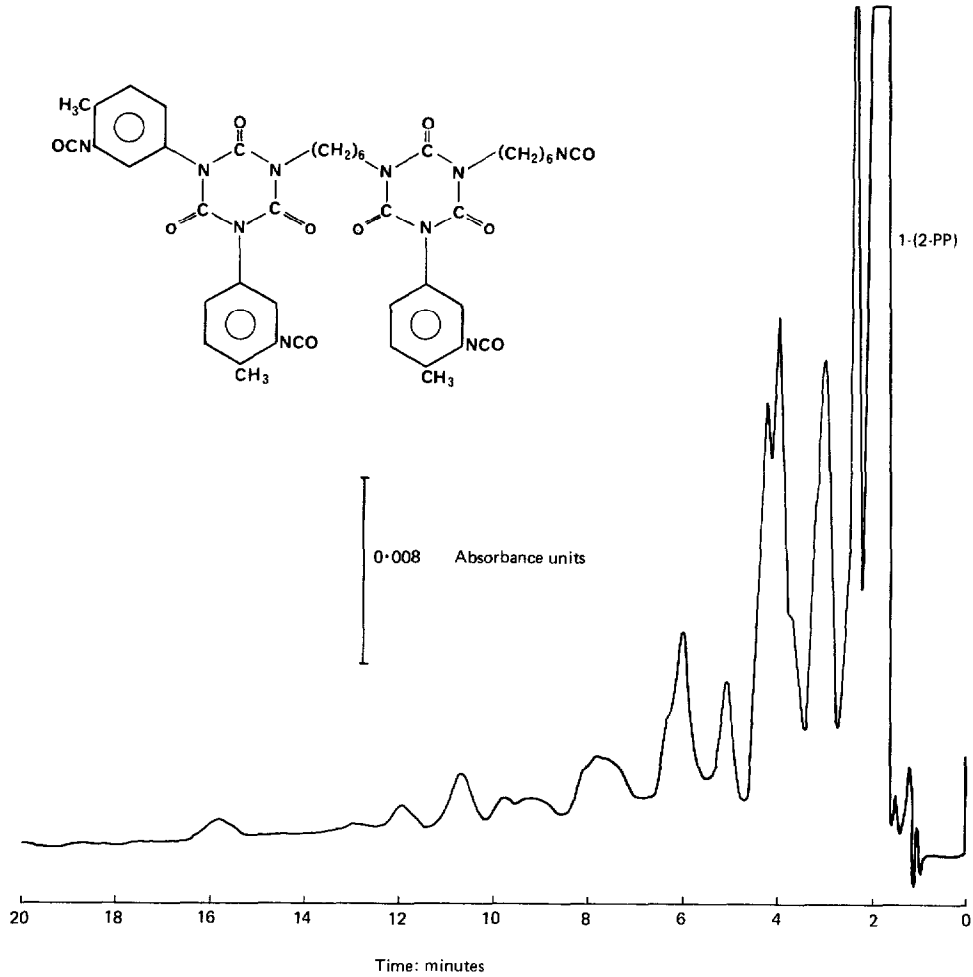

Fig. 5. Chromatogram of 2,4-TDI/HDI-based prepolymer (Desmodur HL) urea derivatives together with excess reagent. Conditions as in Fig. 1, except: sensitivity, 0.04 a.u.f.s.

CONCLUSION

Isocyanate prepolymer mixtures can be separated by reversed-phase HPLC which could form the basis of a method for determining atmospheric prepolymer concentrations in the occupational environment.

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