Journal of Chromatography, 247 (1982) 369–373
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 15,130

Note

Liquid chromatography of some polyurethane polyols

G. BRUCE GUISE* and GEOFFREY C. SMITH
CSIRO Division of Textile Industry, Belmont, Victoria 3216 (Australia)
(Received June 21st, 1982)

Polyurethanes are a diverse family of polymers but all are derived from two types of intermediates, diisocyanates and polyols. A number of chromatographic methods have been described for the analysis of the commonly used diisocyanates but little has been published on polyols even though they represent about 75% (w/w) of most polyurethanes. Most polyurethanes are based on two diisocyanates, 2,4-tolylene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), but a wide range of polyols is used.

The most common type of polyols are poly(propylene oxide) (PPO) and these are manufactured by anionic polymerisation of propylene oxide and polyhydric alcohols (*e.g.* glycerol, propan-1,2-diol, trimethylol-propane). Two side reactions occur in their manufacture: (1) with water (present as impurity) to form PPO diols and (2) chain transfer to monomer which forms allyl alcohol, and this results in the production of PPO mono-ol. Thus, commercial PPO triols contain diol and mono-ol impurities, and the average functionality is below 3.

PPO triols showed a single narrow peak on gel permeation chromatography[1] (GPC), but with thin-layer chromatography (TLC) on silica gel, separation of the mono-ol and diol impurities has been observed[2–4] by Russian workers. This note reports an adaption of the TLC method[2–4] to high-performance liquid chromatography (HPLC). As well as PPO polyols, some other types of polyol were examined. The method was used to follow the reaction of a PPO triol with isocyanates.

EXPERIMENTAL

Polyols were obtained from Bayer (Leverkusen, G.F.R.) and Union Carbide (Melbourne, Australia); the PPO triol (molecular weight, MW = 3000) was Desmophen 3400 (Bayer). The TDI was Desmodur T100 (Bayer) and all other chemicals were analytical grade.

Chromatography was carried out using a 150 × 4.6 I.D. mm column packed with 5-μm LiChrosorb SI 60 (Merck). The pump was a DuPont Model 870, the injection system was supplied by Valco, and the detector was a Shodex SE-11 (Showa Denko KK, Tokyo, Japan) refractive index detector.

After examining a number of solvents and mixtures, we found that ethyl acetate containing a small amount of a polar solvent (methanol or propan-2-ol) gave the best resolution. Russian workers[2–4] used ethyl acetate–water–butan-2-one for their TLC work, but this was too polar for HPLC. Ethyl acetate containing 1%

0021-9673/82/0000–0000/$02.75

propan-2-ol was used in the experiments described below. Samples were injected (10-μl loop) in ethyl acetate and the flow-rate was either 2 ml/min or 0.5 ml/min.

Reactions of the triol with the isocyanates were carried out in the absence of solvent under an atmosphere of nitrogen (see legends to figures for further details).

RESULTS AND DISCUSSION

In the Russian study[2-4] of the TLC of PPO polyols, the extent of adsorption was found to be determined by the number of hydroxyl groups, and for a given

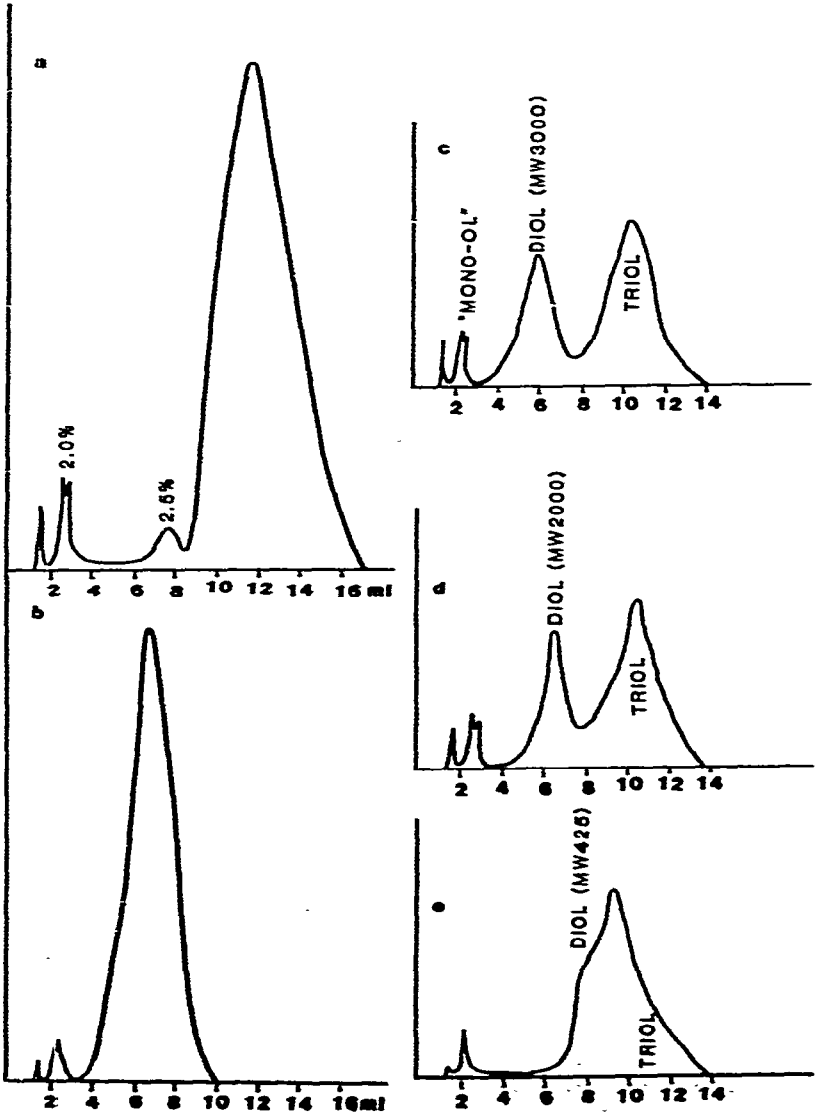

Fig. 1. HPLC of PPO triol (MW 3000) and diols. (a) Triol alone; (b) diol (MW 2000) alone; (c) triol + diol (MW 3000) (3:1); (d) triol + diol (MW 2000) (3:1); (e) triol + diol (MW 425) (3:1).

molecular weight the R_F values were mono-ol > diol > triol, and for a given functionality the R_F value increased with increasing molecular weight. In the present HPLC study, similar trends were assumed, and peaks (Fig. 1a) eluted in front of the mean peak of a MW 3000 triol were assigned to diol and mono-ol on this basis. The mono-ol peak was split, and ahead of it was another peak which appeared to be due to a volatile impurity as it was lost by heating at 80°C for several hours. The resolution of a MW 3000 triol from diols of various molecular weights is shown in Fig. 1c–e. The HPLC method appears to be capable of detecting as little as either 1% diol or mono-ol impurities in PPO triols (that is, assuming equal detector responses of the components). The amount of diol detected in the PPO triol (MW 3000) used in this work was much lower than found[2–4] by TLC in a similar polymer; this difference was attributed to the manufacturing method rather than the analytical method.

A common modification of PPO polyols is to terminate the chains with ethylene oxide units. This replaces the terminal secondary hydroxyls with primary hydroxyls which react faster with isocyanates. On HPLC, such polyols were found to adsorb much more strongly than pure propylene oxide polyols, but they could be eluted by the addition of more isopropanol to the solvent. However, the resultion between triol, diol and mono-ol decreased as the proportion of ethylene oxide units increased, and the amounts of lower functionality impurities could no longer be estimated. The main value of HPLC with ethylene oxide-tipped PPO polyols is to give an indication of the presence of ethylene oxide units.

Some polyester polyols were examined by HPLC. These were similar in polarity to the PPO polyols, and an eluent containing less propan-2-ol was used. A poly(ethylene adipate), MW 2000, showed mainly as a sharp peak; the splitting of the tail of this peak was considered to be due to the separation of the more polar low-molecular-weight oligomers. Some polycaprolactone polyols (from Union Carbide) showed quite extensive splitting and this was assumed to be separation of oligomers; a similar separation of oligomers has recently been reported with hydroxy functional poly(methyl methacrylates)[5].

The HPLC method has been used to follow the reaction of a PPO triol (MW 3000) with isocyanates. In Fig. 2, chromatograms of the reaction product of this triol with different amounts of *n*-butylisocyanate are shown. The peaks in order of elution were assigned to the products of the reaction of the triol with 3, 2 and 1 mol of *n*-butylisocyanate, respectively and were well separated. The GPC method described previously[1] does not resolve these components. The HPLC method could no doubt be used to follow the kinetics of these reactions.

In many applications, polyols are used directly to form polyurethanes, but in others they are first reacted with diisocyanates to form isocyanate terminated prepolymers which are subsequently converted into polyurethanes. The formation of such a prepolymer from PPO triol (MW 3000) and TDI was followed by HPLC (Fig. 3). Control experiments showed that there was negligible reaction of the isocyanates with the propan-2-ol solvent during a chromatogram. After 2 h at 80°C the isocyanate content (determined by reaction with excess amine and titration with acid) of the triol–TDI reaction mixture was constant[1], and this is normally taken to indicate complete reaction. However, HPLC showed that some of the intermediate reaction products were still present. In this reaction, higher-molecular-weight products are formed by chain extension (*e.g.* from 2 mol of triol and 5 mol of diisocyanate), and

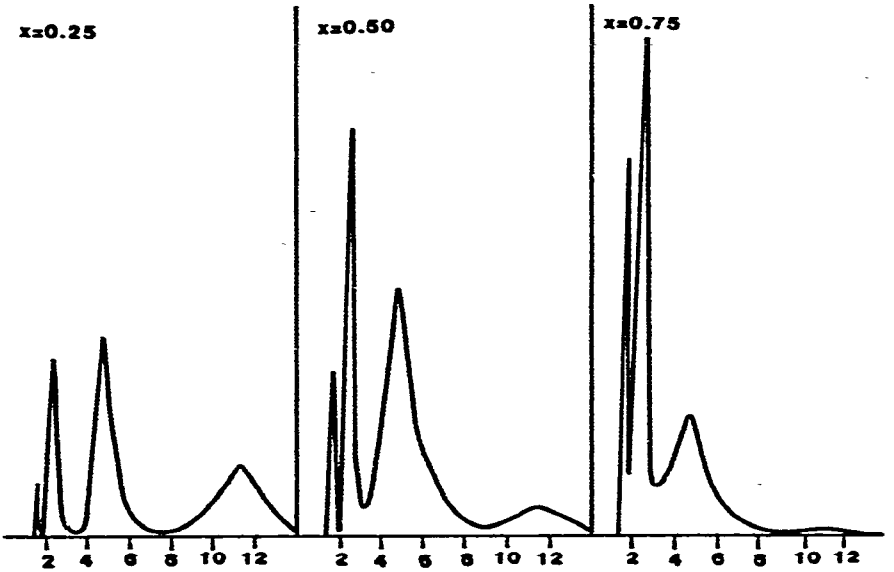

Fig. 2. HPLC of reaction product of PPO triol (MW 3000) and x mol n-butylisocyanate (+ trace of dibutyltin dilaurate catalyst) at 20°C for 16 h.

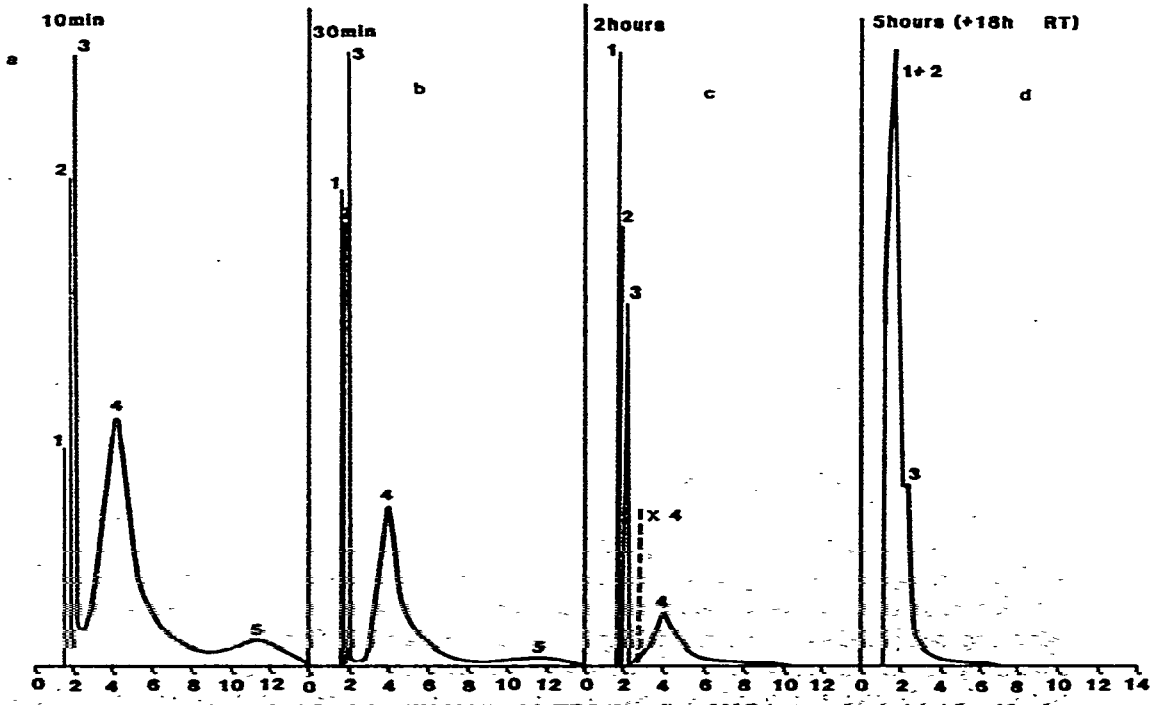

Fig. 3. Reaction product of PPO triol (MW 3000) with TDI (3 mol) at 80°C (no catalyst). (a) After 10 min (attenuation 4); (b) 30 min (attenuation 4); (c) 2 h (attenuations 8 and 2); (d) 5 h (attenuation 8). Peaks: 1 = excluded material; 2 = trisubstituted triisocyanate + TDI; 3 = disubstituted (mono-ol); 4 = monosubstituted (diol); 5 = triol. Horizontal axis denotes time in min, RT = room temperature (20°C).

these products are well resolved by GPC, but not by HPLC. The peak (Fig. 3c) corresponding to the fully reacted product was split on HPLC; this could be due to unreacted TDI, but on the silica used (pore size 6 nm) there is also the possibility of size exclusion of the high-molecular-weight chain extended products.

HPLC thus can be used for the characterization and analysis of polyurethane polyols and to follow their reaction with isocyanates. Lower functionality impurities could be estimated in PPO triols. This HPLC method appears to be a useful complement to GPC studies for polyurethane polyols and the isocyanate terminated prepolymers derived from them.

REFERENCES

1 G. B. Guise and G. C. Smith, *J. Chromatogr.*, 214 (1981) 69.
2 B. G. Belenky, M. D. Valchikhina, I. A. Vakhtina, E. S. Gankina and O. G. Tarakanov, *J. Chromatogr.*, 129 (1976) 115.
3 I. A. Vakhtina, Y. A. Petrakova, V. Pentsel, O. G. Tarakanov, *Polym. Sci. USSR (Engl. Transl.)*, 22 (1980) 1833.
4 K. Knopp, G. A. Gladkovskii, Y. A. Petrakova, U. Pentsel, I. A. Vakhtina and V. S. Lebeder, *Polym. Sci. USSR (Engl. Transl.)*, 22 (1980) 1958.
5 G. D. Andrews and A. Vatyars, *Macromolecules*, 14 (1981) 1603.