Characterization of glycerin-based polyols by capillary electrophoresis

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Abstract

Methods based on capillary electrophoresis (CE) have been developed to obtain the molar mass distribution (MMD) of glycerin-based polyols and details on the presence of mono- and difunctional byproducts in technical samples. Prior to the analyses the hydroxy end-groups of the trifunctional polyols were converted to chargeable and UV-active moieties with phthalic anhydride (PhAH) as the derivatization reagent. With a method of capillary zone electrophoresis (CZE) samples of glycerin-based polyols with average molar masses up to 6000 were separated according to their charge-to-size ratio. The separations were carried out with a buffer solution containing 50% (v/v) acetonitrile and 10 mM sodium tetraborate, and for detection UV absorption at 220 nm was measured. An approximately linear relation between the reciprocal of the effective mobilities and the degree of polymerisation of the glycerin-based polyols was found. Therefore, the proposed CZE system could be used to determine the degree of polymerisation and polydispersity of technical glycerin-based polyol samples. The effect of the presence of sodium dodecyl sulfate (SDS) in the buffer solution on the CE separation of linear polyethylene glycols (PEGs), polypropylene glycols (PPGs) and ethylene oxide–propylene oxide (EO–PO) copolymers with different molar masses was investigated. The interaction between the charged polymer derivatives and SDS ions in solution increased strongly with the degree of polymerisation and the amount PO in the chain of the polymeric compounds. This behaviour made it possible to invert the migration order of EO–PO containing polymers of different size. With a background electrolyte (BGE) composition of 10 mM SDS and 25% (v/v) acetonitrile in borate buffer mono- and difunctional byproducts were separated from the main glycerin-based polyols based on their number of end-groups. Accurate quantities for the mono- and difunctional impurities in technical glycerin-based polyol products were determined.
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1. Introduction

Glycerin-based polyols are generally applied as intermediates in the production of polyurethanes [1]. Glycerin is the starting compound, to which in a batch process chains of ethylene oxide (EO) and propylene oxide (PO) are polymerised. Hence, glycerin-based polyols are trifunctional with three hydroxy end-groups. Different technical polyols can be synthesised with different molar mass distributions (MMDs) (the EO–PO chain lengths), chemical composition distributions (CCDs) (the EO–PO content) and type of end-groups (EO or PO). The most common technical polyols utilized have a molar mass (MM) of 1000–6000 and an EO content of up to 15%.

During the production of polyols in a batch process two types of byproducts (mono- and difunctional) can be formed. Low-MM monofunctional byproducts are produced starting from allylalcohol, which is a result of the rearrangement of propylene oxide. The difunctional byproducts have water as starting compound. After the polymerisation process their chemical architecture is the same as that of linear EO–PO copolymers.

For product properties and performance it is important that the quantity of byproducts in the batches can be determined. Thus far, the only official method for the characterization of polyols is the ASTM D 4274 guideline, which describes titration methods after derivatization with phthalic anhydride (PhAH) [2]. With these methods the total number of hydroxyl end-groups in samples can be determined. Specification of the mono- and difunctional byproducts is not possible.

Capillary electrophoresis (CE) has demonstrated its value as a straightforward and efficient tool for the determination of the degree of polymerisation and polydispersity of synthetic polymers. In a previous study we have shown the use of the capillary zone electrophoresis (CZE) mode for the characterization of linear polyethylene glycols (PEGs) and polypropylene glycols (PPGs) [3]. To provide for charge and detectability both types of linear homopolymers were derivatized with phthalic anhydride before the separation. The PhAH polymeric derivatives migrated with an electrophoretic mobility according to their charge-to-size ratio. A linear relation between the reciprocal of the effective mobility and the degree of polymerisation was obtained for both kinds of polymeric compounds up to an average molar mass of 4000. This made it possible to obtain the MMD of technical PEG or PPG products directly, using the linear plot as a calibration curve. In principle CZE can be also used for the separation of the trifunctional polyols after derivatization with PhAH. However, a complicating factor will be the effect of the CCD of the polyol samples on their mobility in CZE.

Another CE mode applied for the separation of linear PEGs and PPGs, after derivatization with neutral phenyl isocyanate, was micellar electrokinetic chromatography (MEKC) with sodium dodecyl sulfate (SDS) as the surfactant [3]. Hydrophobic interaction between SDS ions and linear polymeric compounds has been observed in several other studies [4-9]. In our work we found that the PPG derivatives showed different interaction with SDS in solution than the PEGs. Not only the hydrophobic end-groups (phenyl isocyanate) but also the PPG chain interacted with the SDS ions. In the experimental work described in this paper the interaction between SDS ions and the PPG chains in derivatized glycerin-based EO–PO polyols was used to separate mono- and difunctional byproducts in technical samples.

2. Experimental

2.1. Chemicals

Technical glycerin-based polyols with different MMDs and CCDs were provided by Dow Benelux (Terneuzen, The Netherlands). Linear PEGs, PPGs, EO–PO copolymers and the internal standard (IS) pentaethylene glycol were obtained from Aldrich (Steinheim, Germany). The monofunctional allyl alcohol–PO–EO adducts were a gift from Shell (Amsterdam, The Netherlands). Data on the samples used, as provided by the suppliers, are given in Table 1.

Table 1
Data on the polymer samples as provided by the suppliers

Sample	Functionality	Type	MM (Da)	EO (%, w/w)
Polyol 1000	3	PO	1000	–
Polyol 3000	3	PO–EO	3000	10
Polyol 4000	3	PO	4000	–
Polyol 6000	3	PO–EO	6000	15
Co–EO–PO 1900	2	EO–PO–EO	1900	50
Co–EO–PO 2000	2	EO–PO–EO	2000	10
Co–EO–PO 2500	2	Random	2500	75
Allyl alcohol 1000	1	Random	1000	13

At the start of the experiments a fresh lot of PhAH was obtained from Acros Organics (Geel, Belgium), which was stored in an excicator. Imidazole and 1,4-diazabicyclo[2,2,2]octane (DABCO) both used as catalyst were also obtained from Acros Organics. Borate buffers applied were prepared by dissolving disodium tetraborate decahydrate (Merck, Darmstadt, Germany) in sub-boiled demi-water. All other chemicals used were of analytical grade purity and obtained from certified suppliers.

2.2. CE system

CE experiments were performed on an Agilent CE system (Agilent Technologies, Waldbronn, Germany) equipped with a photo diode-array (PDA) detector. The Agilent Chemstation software was used for instrument control and data acquisition. For detection of the PhAH polymer derivatives UV absorption was measured at a wavelength of 220 nm with a bandwidth 8 nm.

Fused silica capillaries of 75 μm i.d. × 375 μm o.d. were obtained from Composite Metal Services (The Chase, UK). The effective length of the capillaries installed were 45 cm and the total length 53.3 cm. Injections were performed by pressure typically at 20 mbar for 3 s. Voltages of 25 kV were applied. All analyses were carried out at 25 °C.

2.3. Derivatization

Approximately 0.1 mmol of the polymeric compounds were weighed in a 3 ml vial, and 1 ml of a reagent mixture containing an acetonitrile solution with 1 M PhAH, 0.6 M DABCO and 0.3 M imidazole. The polymer solution was spiked with 2 μl penta-ethylene glycol, which acted as a marker for the mobility. The vial was placed in an oven at 100 °C for 30 min. After cooling, 100 μl of the reaction mixture was added to 1 ml of an acetonitrile–water (70:30) mixture, and this solution was heated at 55 °C for 30 min. Finally, this solution was diluted 1:1 with the buffer solution as used for the separation. Following this procedure, the sample solutions injected in the CE system had polymer concentrations of approximately 5 mM.

3. Results and discussion

3.1. Determination of the MMD of the glycerin-based polyol samples

Recently, we have demonstrated that CZE can be a valuable tool to study the MMD of linear PEG and PPG homopolymers [3]. Depending on the composition of the separation buffer small differences were found between the effective mobilities of PhAH derivatized PEGs and PPGs with the same monomer number. Since such differences would complicate the analysis of EO–PO copolymers, we have tried to find conditions where the mobility differences between PEG and PPG homopolymers were minimal. The best results in this respect were obtained using a background electrolyte (BGE) containing 50% (v/v) acetonitrile in sodium tetraborate buffer at a total ionic strength of 20 mM. As is shown in Fig. 1, the effective sizes of PEG and PPG chains (observed as the reciprocal of their mobilities) were very similar in this buffer solution for chain lengths up to 50 monomers (MM 2200–2900). Only for longer polymeric chains significant differences in the mobilities of PEG and PPG homopolymers were observed.

The separation of a tri-block (EO–PO–EO) copolymer 1900, with an average EO content of 50% (w/w) is shown in Fig. 2. The electropherogram was translated into the monomer-number distribution using the quasi-linear relation for the reciprocal mobility and degree of polymerisation obtained for the PPGs. The oligomeric peaks were only slightly broader than the peaks obtained with the homopolymers, as a result of the inherent composition variation in chains with a specific monomer number.

The same procedures for derivatization and separation were applied to the monofunctional allyl alcohol–PO–EO adducts and glycerin-based polyols. For the first mentioned type of compounds, PhAH derivatization yielded single-charged derivatives, while with the conversion of the glycerin-based polyol samples triple-charged compounds were formed. All investigated monofunctional adducts and
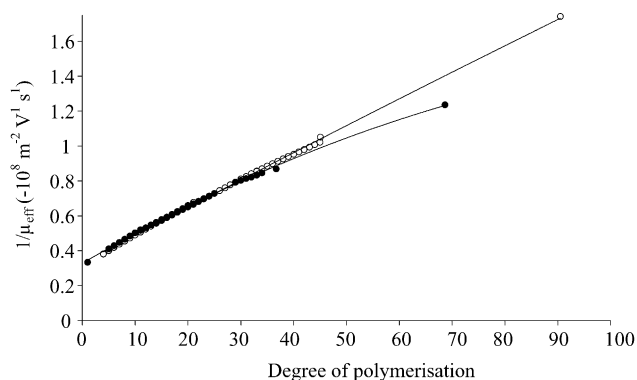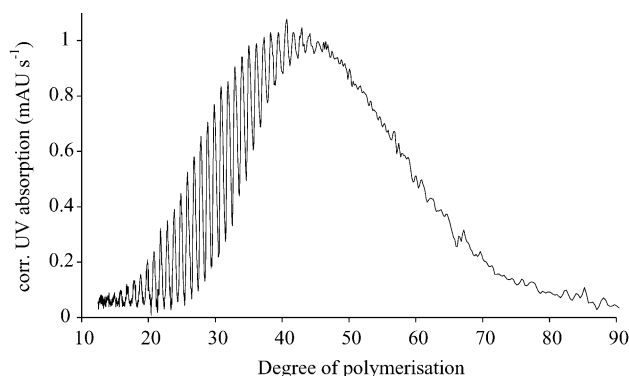

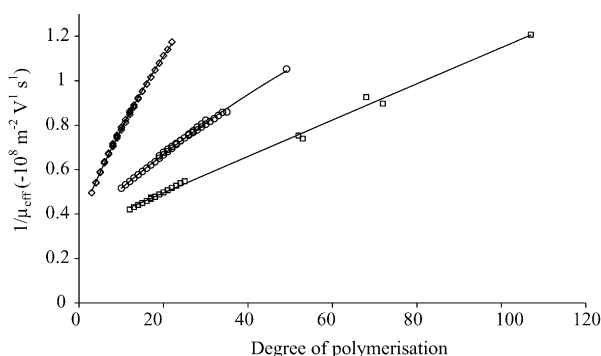Fig. 2. The monomer-number distribution of an EO–PO copolymer of MM 1900 with 50% (w/w) EO as calculated from an electropherogram.

Fig. 3. Relation between the reciprocal of the effective mobilities of PhAH derivatized monofunctional allyl alcohol–EO–PO adducts ($\diamond$), difunctional EO–PO copolymers ($\bigcirc$), and trifunctional glycerin-based polyols ($\square$) as a function of their degree of polymerisation. For conditions see Fig. 1.

the low-MM glycerin-based polyols could be separated into individual peaks representing chains with a specific degree of polymerisation (*n*). The effective mobilities of the monofunctional oligomers were clearly lower, and those of the polyol derivatives clearly higher, than the mobilities of linear (double-charged) EO–PO copolymers with the same number of monomers (Fig. 3). Both the single- and the triple-charged derivatives yielded approximately linear plots for the reciprocal of the effective mobility and the degree of polymerisation.

For the glycerin-based polyol samples the plot was used to convert electropherograms obtained experimentally into the monomer-number distribution of the samples, using a laboratory-written algorithm developed in Excel, assuming a quadratic relation between the reciprocal of the mobility and the degree of polymerisation. In Table 2 the results for the

Fig. 1. Relation between the reciprocal of the effective mobilities of PhAH derivatized PEGs ($\bigcirc$), and PPGs ($\bullet$) and their degree of polymerisation. BGE: 50% (v/v) acetonitrile in 10 mM borate buffer. Voltage: 25 kV.

Table 2
Data on the MMD of the glycerin-based polyol samples

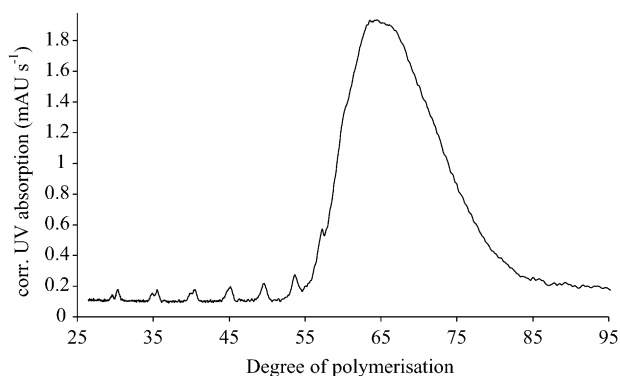| Sample	MM		Polydispersity experimental
	Supplier	Experimental	
Polyol 1000	1000	1150	1.03
Polyol 3000	3000	3050	1.03
Polyol 4000	4000	4000	1.02
Polyol 6000	6000	6100	1.02

Fig. 4. Translation of an electropherogram as obtained by CZE into a monomer-number distribution for the polyol 4000 sample.

polyols are compared with the nominal molar mass values as given by the supplier. A good correlation was found, with deviations for the number-average molar mass value smaller than 6%. It should be noted, however, that the calibration plot was partly based on some of the same samples, so that the accuracy of the data for the high molar mass range cannot be assessed from this.

With some of the polyol samples a group of small peaks showed up in the electropherograms, which were clearly not related to glycerin-based trifunctional polymers. An example is shown in Fig. 4, which gives the translation of an electropherogram into a monomer-number distribution calculated for polyol 4000. As will be shown below, such peaks came from mono- or difunctional byproducts in the technical polyol samples.

3.2. Determination of byproducts in glycerin-based polyols

As was described above, PhAH derivatized mono-, di- and trifunctional EO–PO polymeric compounds had strongly different electrophoretic mobilities in a CZE system. Given the generally low polydispersity of this type of polymers, it would be relatively simple to obtain a separation of trifunctional polyols from mono- and difunctional byproducts with similar average molar masses. As an illustration, Fig. 5A shows an overlay of the electropherograms obtained with monofunctional adducts, a PPG homopolymer and a glycerin-based polyol all with an average molar mass of approximately 1000. For clarity, the y-axes have been scaled to give almost similar peak heights. Unfortunately, it is to be expected that the mono- and difunctional byproducts in a real polyol sample will have lower molar mass values than the main polyol itself. Therefore, Fig. 5B shows a more realistic picture. An overlay is shown of the electropherograms obtained for a monofunctional adduct with an average MM of 1000, a difunctional PPG sample with an average MM of 2000, and a trifunctional glycerin-based polyol with an average MM of 3000. Unfortunately, since the differences in charge between the three types of polymers were now largely counteracted
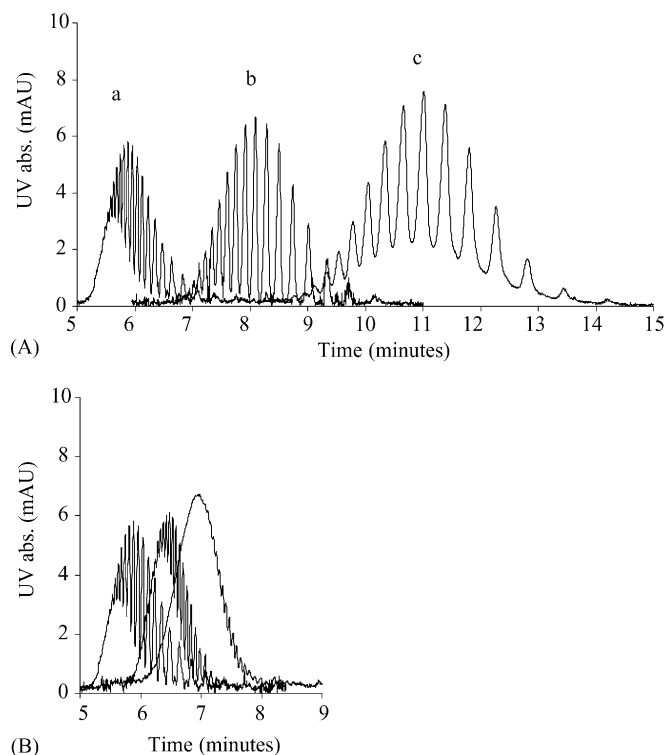

Fig. 5. Overlay of the electropherograms of (A) allyl alcohol adducts (a), EO–PO copolymer (b) and glycerin-based polyol (c) with all MMs of 1000, and (B) allyl alcohol adducts of MM 1000 (1), an EO–PO copolymer of MM 2000 (2), and a glycerin-based polyol of MM 3000 (3). Conditions as in Fig. 1.

by differences in size, a strong overlap between the three sets of peaks was observed.

Preliminary experiments showed that the presence of SDS in the separation buffer had effect on the mobilities of the charged PhAH derivatives of the polymers used in this study. Therefore, we investigated the possibility to use the interaction of SDS ions with the polymeric chains to improve the separation of mono- and difunctional byproducts from the glycerin-based polyols.

First, the mechanism of interaction between SDS ions and double charged PPG derivatives was investigated. Separations of a PPG 2000 standard, derivatized with PhAH, were performed using BGEs with various concentrations of SDS (0–5 mM) and various percentages of acetonitrile (25–50%, v/v). The ionic strength of the separation medium was kept constant at 20 mM by adapting the concentration of the borate buffer. Fig. 6 shows the influence of the SDS concentration on the (peak-top) mobility of the PPG 2000 standard. The effective mobility increased approximately linear with the SDS concentration and the influence of SDS decreases with increasing the organic modifier content. Results for 25, 30 and 35% (v/v) acetonitrile are shown. At lower acetonitrile percentages problems with the solubility of the PPG derivatives were encountered; at higher acetonitrile fractions (up to 50%, v/v) a gradual further decrease of the effect of SDS on the mobility of the polymer derivatives was found. The results
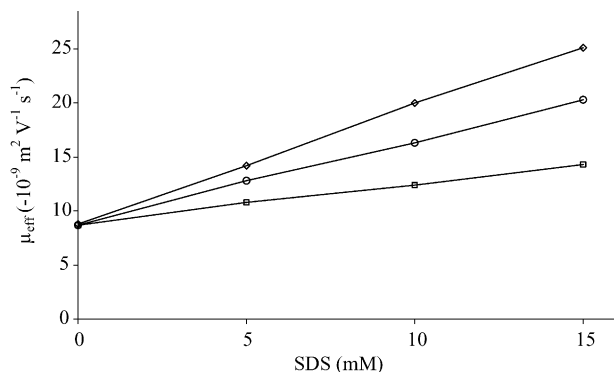
Fig. 6. Effect of the SDS concentration and percentage (v/v) acetonitrile 25 (◇), 30 (○), and 35% (□) on the effective mobility of the homopolymer PPG 2000.

of these experiments indicate that the separation mechanism of SDS and polymeric compounds is based on a regular hydrophobic interaction mechanism. No evidence was found for a minimum concentration below which the SDS has no influence. Apparently, there is no well-defined critical micelle concentration in the acetonitrile–water mixtures studied, with an acetonitrile fraction of minimal 25% [10].

Next, the effect of the CCD (% EO) of the polymeric compounds on the interaction with SDS ions was studied. Homopolymers of PEG and PPG, as well as a number of tri-block EO–PO–EO copolymers, all with an average molar mass of approximately 2000, were derivatized with PhAH and separated in solutions with 30% (v/v) acetonitrile and varying concentrations of SDS. As is shown in Fig. 7, the PEG derivative (100% EO) shows an almost negligible interaction with SDS. The degree of interaction of SDS ions with the copolymers increases with the relative length of the PO block in the polymeric chains. There was no significant difference found between triblocks of the type EO–PO–EO and PO–EO–PO with the same EO–PO ratio (data not shown). The effective mobility of the derivatives of the PPG homopolymer (0% EO) increased most strongly with increasing SDS concentration.
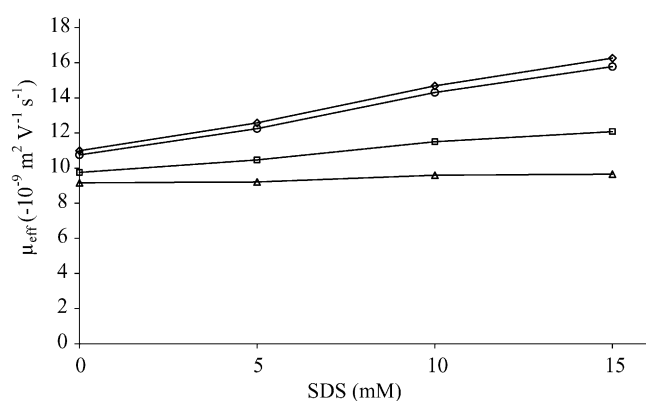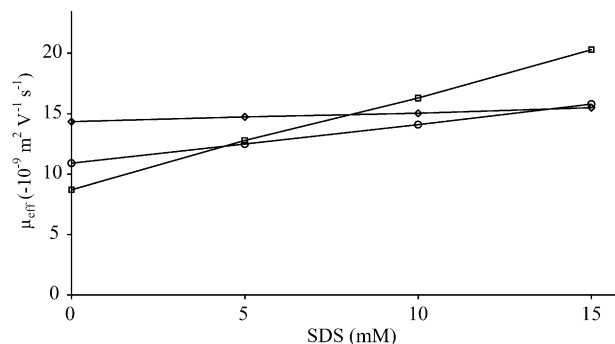

Fig. 8. Effect of the SDS concentration on the effective mobilities of PPGs with average MMs of 1000 (◇), 2000 (○), and 4000 (□).

In Fig. 8 the SDS-effect is shown for PhAH derivatized PPGs with average MM values of 1000, 2000 and 4000. It was found that the influence of SDS on the effective mobility increased strongly with the length of the PPG chains. At high SDS concentration (15 mM) the migration order of PPGs with different chain lengths can even be inverted (Fig. 9). To the blend penta-ethylene glycol was added as a mobility marker. Additional low-mobility peaks were observed in all electropherograms, probably caused by impurities or byproducts from the derivatization reagent. The symmetric peak (the second peak in Fig. 9 or Fig. 11) was regarded as the EOF marker. The inverted migration order is of importance for the analysis of technical polyol samples, where high-MM trifunctional compounds are to be discriminated from lower MM mono- and difunctional byproducts. Similar experiments were performed with glycerin-based polyols with different MMs of 1000–6000. The polyol samples contained mostly PO, with EO contents up to 15% (w/w). With these samples it was also found that the SDS influence increased with the MM value (Fig. 10).

When using a buffer with 15 mM SDS the mass selectivity of the separation system was largely lost, and all polyols except the smallest (with a MM of 1000) eluted at almost the same migration time. Moreover, the effective mobility of the

Fig. 7. Effect of the SDS concentration on the effective mobilities of difunctional EO–PO polymers (MM ∼ 2000) with CCDs of 0 (◇), 10 (○), 50 (□), and 100% (△) (w/w) EO.
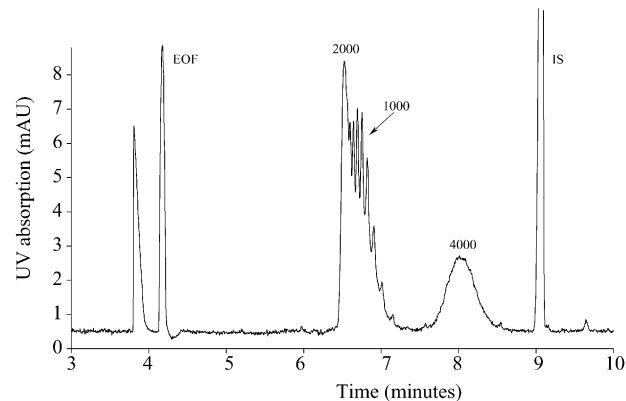

Fig. 9. Separation of a blend of PPG 1000, 2000 and 4000 using a BGE of 15 mM SDS and 30% acetonitrile in 2.5 mM borate buffer. Voltage: 25 kV. Pentaethylene glycol was used as IS.

Table 3
Recovery of byproducts added to polyol 3000

Amount (%)	Blank		1		2		3		4	
	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
1 –OH	–	3	2	5	4	6	6	7	9	10
2 –OH	–	8	4	11	8	14	13	18	17	21

high-MM trifunctional polyols was significantly increased compared to the mobilities of the mono- and difunctional byproducts. In the electropherogram of real technical polyols the monofunctional byproducts were baseline separated. However, the difunctional impurities overlapped slightly with the main glycerin-based polyol. We have investigated different possibilities to improve the resolution of the difunctional compounds and trifunctional polyols. Increasing the SDS concentration did not help much. With a lower acetonitrile concentration (25%, v/v) a slightly higher resolution was obtained when the SDS concentration was decreased to 10 mM. As an alternative for SDS, the more hydrophobic sodium tetradecyl sulfate (STS) at concentrations of 1–10 mM was tested. It was found that STS interacted much stronger with the polymer-derivatives than SDS. The highest selectivity was found using an STS concentration of 2.5 mM. Still, the separation of the double-charged byproducts from the main polyol was comparable to that obtained with 10 mM SDS.

It can be concluded that a buffer composition containing 10 mM SDS and 25% acetonitrile in 5 mM borate buffer gives the best separations, as is illustrated in Fig. 11 that shows the analysis of the technical polyols 3000 and 6000. In the polyol 3000 both the mono- and difunctional byproducts were detected, while the polyol 6000 contained only the monols.

To validate the CE method for the quantification of the byproducts in technical polyol products, recovery experiments have been performed. To the polyol 3000 sample different amounts of EO–PO copolymer 2000 and allyl alcohol 1000 were added to represent the potential byproducts. From the data obtained experimentally the percentage of the number of hydroxyl-groups present in mono- and difunctional
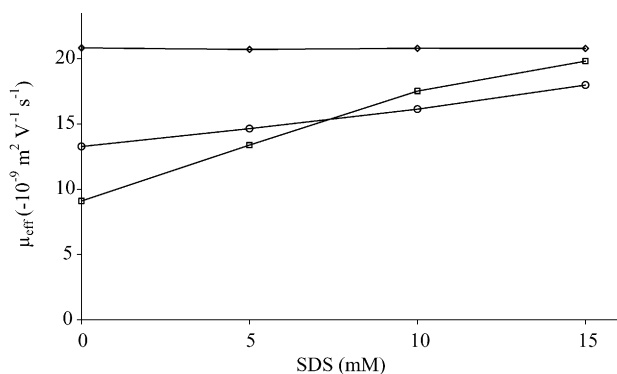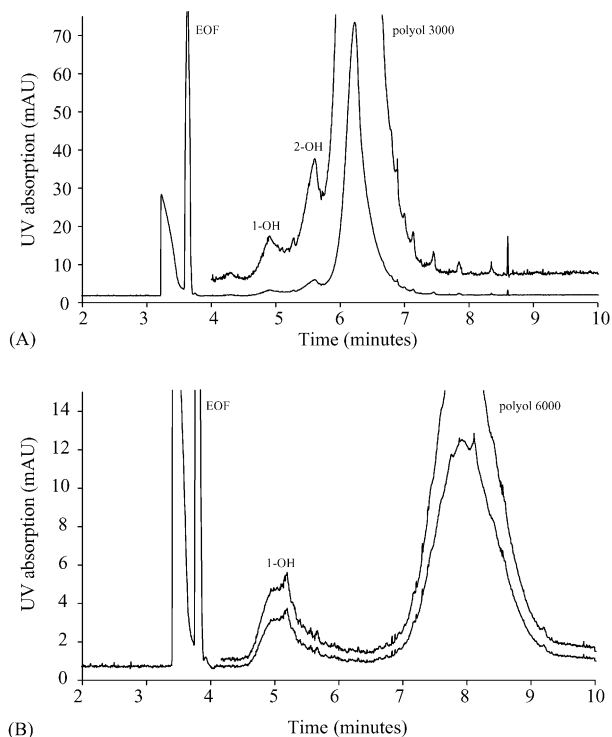

Fig. 11. CE separations of technical (A) polyol 3000, and (B) polyol 6000 samples after derivatization with PhAH under optimised conditions. BGE: 10 mM SDS and 25% acetonitrile in 5 mM borate buffer. Voltage 25 kV.

compounds to the total number of hydroxyl-groups was calculated. Results are given in Table 3. Good correlations were found, taking into account the presence of mono- and difunctional byproducts in the technical polyol sample itself.

4. Conclusions

It has been shown that CE is a valuable tool for the characterisation of polyol samples. For the required derivatisation a procedure is described that is quantitative and fast compared to previously used methods [3]. First, CE can be used to determine the MM distribution of the main (trifunctional) compound. For this, a standard instrument and standard CZE conditions can be used. The straightforward relation between the observed mobility and the degree of polymerisation makes calibration easy and reliable; at least for the lower end of the MM range of interest calibration can even be based on peak counting, and the availability of calibration standards is not a prerequisite.

Fig. 10. Effect of the SDS concentration on the effective mobilities of glycerin-based polyols with average MMs of 1000 ($\Diamond$), 3000 ($\bigcirc$) and 6000 ($\square$).

Secondly, CE can be used to quantify the concentrations of the mono- and difunctional byproducts often present in polyol samples. For this, the same instrumentation and the same (derivatized) samples can be used. Only a different (SDS containing) background electrolyte has to be used.

With two simple experiments, both with a run-time of approximately 10 min, the main parameters for the quality of polyol samples can be determined.

Acknowledgement

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