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Analysis of organosilicone copolymers by gradient polymer elution chromatography with evaporative light scattering detection

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Abstract

Organosilicone copolymers have found numerous applications in the cosmetics, detergent and coating industries. Coupling a polar polymer (like polyglycols) to a non-polar silicone gives anchorage and emulsification capabilities to the polymer. When coupling a silicone polymer to a polyglycol, the copolymer formed differs from the starting polymers by a single bond which is often difficult to evidence using spectroscopic techniques such as NMR or infrared, especially when the polymers have a high molecular mass. Gradient polymer elution chromatography (GPEC) coupled to an evaporative light scattering detector was developed for the characterization of copolymers based on their chemical composition distribution. Different block and graft polyglycol–silicone copolymers were successfully characterized by GPEC and residual homopolymers have been easily quantified.

Keywords: Gradient polymer elution chromatography; Organosilane compounds; Polymers; Polyglycols; Polydimethylsiloxane

1. Introduction

Organosilicone copolymers have found numerous applications in the cosmetic, detergent and coating industries. In order to make them compatible with water, the silicone must either be emulsified or coupled to a water-soluble polymer. Coupling a polar polymer (like polyglycols) to silicone gives anchorage and emulsification capabilities to the polymer.

The characterized polyglycol–silicone copolymers are graft or block copolymers with a polydimethylsiloxane (PDMS) backbone and polyglycol side chains or end groups. The chemical and physical properties of polyglycol–silicone copolymers can be tailored to suit various applications by changing their chemical composition: i.e. either by changing the chain length of the PDMS and polyglycols, by modifying the glycol/silicone ratio or by adapting the number of polyglycol side chains for graft copolymers.

The performance of these copolymers is dependent upon the choice of the homopolymers (i.e. their molecular mass, but also their molecular mass distribution) and the chemical composition distribution in the final copolymer sample. Most copolymer samples contain residual unreacted homopolymers (i.e. PDMS and polyglycols).

When coupling a polyglycol to a silicone polymer, the copolymer formed differs from the starting polymers by a single bond which is often difficult to evidence using spectroscopic techniques such as NMR or infrared, especially when the molecular mass of the polymer is high. Techniques such as size-exclusion chromatography (SEC) can measure

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the molecular masses of polymers but do not give any accurate information on the chemical composition of the final copolymer sample.

Recent development in liquid chromatography using non-exclusion liquid chromatography (NELC) have shown the possibility of separating synthetic copolymers according to their chemical composition [1]. Since most NELC techniques require the use of gradient solvent elution, UV detectors have been exclusively used in the past. Therefore, most copolymers reported in the literature are styrene based copolymers [1]. In recent years, new developments in evaporative light-scattering detection (ELSD) systems have made them more sensitive, more reliable and more user-friendly. These detectors are now more and more used for the high-performance liquid chromatography (HPLC) characterization of non-UV absorbing copolymers.

Gradient polymer elution chromatography (GPEC) covers the application field of polymers and gradient separation technology and is distinguishable from other mechanisms of gradient HPLC separation [2]. In general, polymer separation by GPEC is based on a precipitation–redissolution mechanism. The major difference versus other HPLC separations is that with GPEC, interactions with the stationary phase are minimized. GPEC coupled to ELSD is shown to be adapted to the analysis of organosilicone copolymers. It enables the separation and quantification of unreacted homopolymers and the characterization of a copolymer based on its chemical composition distribution.

This paper describes the evaluation of GPEC coupled to ELSD for the characterization of polyglycol–silicone copolymers.

2. Experimental

2.1. GPEC apparatus

A Perkin-Elmer chromatography system (Norwalk, USA) was used to run the analyses. This HPLC equipment consists in a series 410 LC gradient pump, a SEC-4 solvent environmental control flushed with helium and a series LC 127 autoinjector. Data collection was carried out by the Perkin-Elmer TURBOCHROM data acquisistion system via a Nelson interface. The gradient pumping system lag volume was determined as 6 min to the column inlet.

Two gradient systems were used: (1) residual silicone and copolymer were precipitated in water and then gradually eluted by increasing the amount of an organic solvent and (2) residual polyglycol and copolymer were precipitated in an alkane solvent and then eluted by increasing the amount of a more polar solvent.

The gradient profile used in all measurements was: 2 min with 100% non-solvent, 5–10 or 15 min, linear to 100% solvent, 5 min with 100% solvent and 2 min, back to 100% non-solvent. The flow-rate was 1 ml/min. The injection volume was 10 μl.

Two ELSD instruments were used in the course of this study: an Alltech Model 500 (Deerfield, USA) or a Sedex 55 (SEDERE, Alfortville, France). The major difference between both ELSD systems is that in the Sedex detector the mobile phase is nebulized at room temperature in a special spray chamber, in which larger droplets are trapped, while in the Alltech instrument the entire aerosol is carried out through the heated drift tube [3]. For both detection systems, nitrogen was used as carrier gas, and the pressure at the nebulizer was set to 2.0 bar.

The chromatographic separations were carried out on short columns, ususally guard-columns in order to minimize column interactions. Different Waters guard columns (Milford, USA) were used: Nova-Pak cyanopropyl (CN), silica (Si) guard columns (20× 3.9 mm, pore size 6 nm, particle size 4 μm).

2.2. Samples

The copolymers investigated were synthesized by grafting or coupling reactions. Branched (graft) polyglycol–silicone copolymers were prepared by reaction of different polyglycols allyl end-blocked at one side to a PDMS polymer containing pendant Si–H groups. Block polyglycol–silicone copolymers were prepared by coupling reaction of a hydroxyl end-blocked PDMS with polyglycols hydroxyl-ended at one side. The average chemical composition of the samples were determined by proton nuclear magnetic resonance spectroscopy.

Sample solutions for direct injection into the

column were prepared at 0.5% (w/w) ±0.1 concentration in tetrahydrofuran (THF).

2.3. Solvents

Clean solvents with only trace amounts of non-volatile impurties are required for ELSD detection [4].

HPLC-grade solvents (Rathburn, UK) were used to prepare mobile phases. THF without antioxidants (Rathburn) was used and kept under helium to prevent peroxide formation. High-quality water (i.e. 18 MΩ.cm and free of organic impurities) was prepared by the Milli-U6 water purification system (Millipore, Bedford, USA).

3. Results and discussion

Block and graft polyglycol silicone copolymers were analysed by GPEC in order to provide qualitative information on their chemical composition and quantitative information on residual homopolymers. The GPEC process relies on initial precipitation of copolymer (in solution at 0.5% in THF) on the column by carrying the elution with a non-solvent, followed by redissolution in a gradient of good solvent in the non-solvent. In general, interactions between polymers and the stationary phase are minimized by GPEC.

3.1. Quantitative aspects

During GPEC separation, the signal of non-volatile components detected by ELSD is mainly a function of the concentration but is only slightly dependant on the nature of the analyte. The detector response for different copolymers and polymers in solutions has been recorded by direct injection through the nebulizer. Results presented in Table 1 confirm that the ELSD response does not depend on the polymer nature.

ELSD response can be affected by the composition of the mobile phase. Fig. 1 shows the peak areas obtained for polyglycol standards as a function of concentration in two different solvents. It is clear that using water as mobile phase instead of THF–methanol results in a loss of sensitivity, probably due to water being only partially nebulized at 40°C. Most organic solvents in general give similar responses.

Table 1
ELSD detector response versus polymer nature; solutions at 0.5% concentration in solvent THF–methanol (80:20)

Samples	Integrated peak area ($mV\ s \cdot 10^6$)
PDMS	26.7
Polyglycol	20.0
Polymethylmethacrylate (PMMA)	21.3
PMMA–block PDMS copolymer	21.8
Polyglycol block PDMS copolymer	23.9

GPEC coupled to ELSD enables the quantification of unreacted homopolymers in copolymer samples. However, ELSD must be calibrated very carefully in order to yield reliable results. ELSD response can be expressed by an exponential function. The linearity for PDMS and polyglycol homopolymers has been verified by r^2 values for the log/log plots of peak area versus concentration. The correlation coefficients wers shown to be higher than 0.99 in different gradient solvent systems.

Due to the exponential character of the detector, the peak area will not only be a function of the concentration but also of the peak width. Table 2 shows that signal height and peak area decrease with increasing gradient time in absence of saturation effect (i.e. 1000 mV); this decrease in peak area is accompanied by an increase in signal broadening. The large band width observed is due to the low molecular mass of polyglycols. This means that the polymer, due to its molecular mass distribution, will not elute at a specific solvent/non-solvent composition but over a range of solvent/non-solvent composition. This is in accordance with theory which predicts that the solubility of low-molecular-mass polymers is a function of their molecular mass. On the other hand this highlights the fact that although ELSD system is a universal detector with constant response factors, precautions have to be taken when using it for quantitative purposes.

3.2. Chromatographic separation of graft copolymer samples on a medium polarity column

Graft copolymers are obtained by coupling a PDMS backbone containing 10 mol% of SiH units

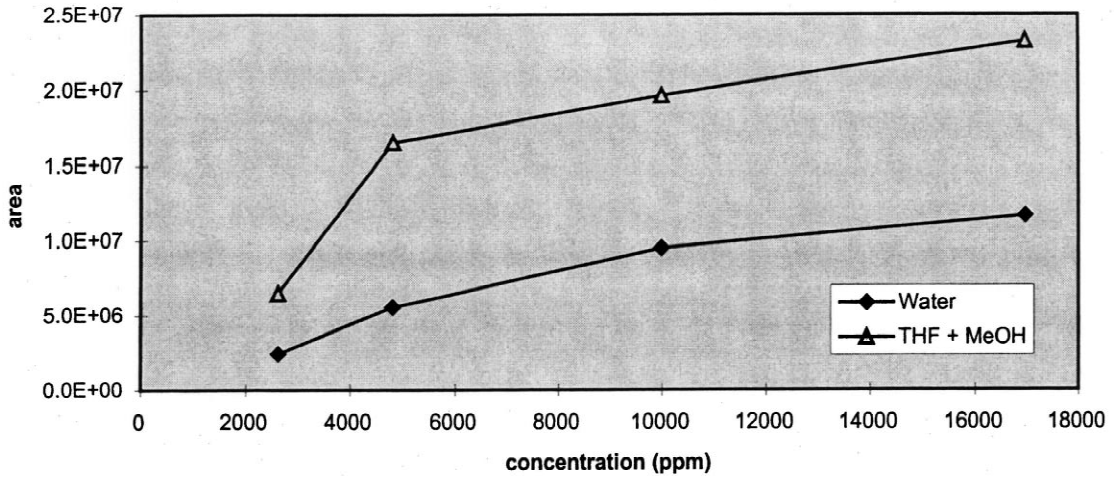

Fig. 1. Peak areas of polyglycol standards as a function of concentration, as obtained from isocratic LC in two mobile phases (i.e high purity water and THF–methanol, 90:10 at 40°C evaporator temperature. The column is Nova-Pak CN guard column.

with polyglycol homopolymers of different chain lengths [i.e. CH_2=CH$(EO)_n$OH with $n=4$, 7, 12 or CH_2=CH$(EO)_6(PO)_6$OH] (EO = ethylene oxide, PO = propylene oxide) in the presence of a Pt-based catalyst. Because of their huge difference in polarity, all the constituents (i.e. starting residual homopolymers and the copolymer) of the synthesis cannot be precipitated in a common non-solvent.

In order to separate the copolymer from residual homopolymers, the copolymer and one homopolymer have been precipitated in a non-solvent in which the second homopolymer is soluble. In this case, two gradient systems can be considered: either residual PDMS and copolymer are precipitated in a polar solvent and then eluted by increasing the amount of an organic solvent, or the polyglycol and copolymer are precipitated in an alkane solvent and then eluted by increasing the amount of a more polar solvent.

Without any interaction with the stationary phase, GPEC separation is only based on polymer solubility in the gradient. A medium polarity column (cyanopropyl, CN) which only has low interactions with both polar and non-polar constituents of the copolymer sample is used.

Table 2
Relation between peak heights, areas, signal bandwidth of polyglycol in function of the gradient time

Elution mode and gradient time	Polyglycol concentration (ppm)	Peak height (mV)	Band width (s)	Peak area (mV s·10^7)
Isocratic:	2500	680	9	0.7
THF–methanol	5500	1000	15	2.0
(80:20)	16 000	1000	23	2.2
Gradient 3 min	2500	240	27	0.6
TMP to	5500	810	36	2.8
THF–methanol (80:20)	16 000	1000	66	7.2
Gradient 5 min	2500	130	48	0.5
TMP to	5500	330	54	1.8
THF–methanol (80:20)	16 000	1000	90	7.5
Gradient 10 min	2500	30	90	0.3
TMP to	5500	110	96	1.0
THF–methanol (80:20)	16 000	560	105	4.1

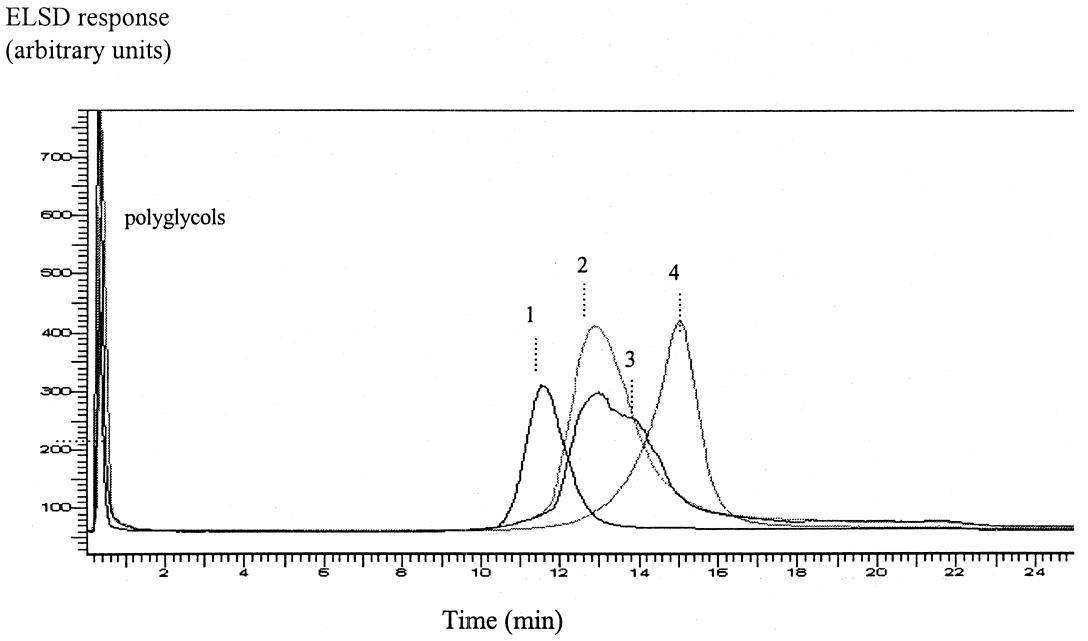

Fig. 2. Gradient chromatograms of graft copolymers with grafted CH_2=CH(EO)$_{12}$OH units (1); CH_2=CH(EO)$_7$OH units (2); CH_2=CH(EO)$_4$OH units (3) and CH_2=CH(EO)$_6$(PO)$_6$OH units (4). Gradient from 100% water to 100% isopropanol. Nova-Pak CN guard column.

Fig. 2 show chromatograms for four graft copolymers of different composition. The chromatograms show two peaks. The first peak is assigned to ungrafted polyglycol homopolymer which is soluble in the starting eluent and elutes in the dead volume. The second peak is the copolymer which is not soluble in the non-solvent, precipitate in the column and elutes in the solvent gradient. No residual PDMS homopolymer is observed to be present in analysed samples.

The copolymer retention time depends on the polarity of polyglycol chains grafted on the PDMS backbone, as shown in Fig. 2. The copolymer with long grafted polyglycol chains (i.e., with $n=12$) elutes the first, whereas the copolymer with short grafted chains (i.e., $n=4$) and thus less polar elutes later in the gradient. The copolymer with grafted $(EO)_6(PO)_6$ chains elutes even later because of the lower polarity of PO units. This is confirmed in Table 3 with the comparison of titrimetric cloud-points (i.e. turbidimetric titration tests) and copolymer retention times. The cloud-point is the solvent/non-solvent composition of the eluent gradient for which the copolymer becomes soluble and is expressed in percentage of non-solvent (i.e.%NS) [3]. Titrimetric cloud-points are determined by titrating dissolved polymers with a non-solvent which precipitates the polymers. Titrimetric cloud-points of the

Table 3
Titrimetric cloud-points (percentage of non-solvent, %NS) and retention times of graft copolymers

Copolymer samples	Cloud point (%NS)	t_R (min)
1. Copolymer with grafted CH_2=CH(EO)$_{12}$OH units	63	11.53
2. Copolymer with grafted CH_2=CH(EO)$_7$OH units	55	12.87
3. Copolymer with grafted CH_2=CH(EO)$_4$OH units	54	12.97
4. Copolymer with grafted CH_2=CH(EO)$_6$(PO)$_6$OH units	51	15.05

copolymer and starting homopolymers enable to predict their retention time in a gradient elution, in the absence of interactions between polymers and the stationary phase.

For high-molecular-mass copolymers, the cloud-point is mainly a factor of the nature of the polymer and is only slightly changing with its molecular mass. On the other hand, for low-molecular-mass copolymers, GPEC separation is based on their chemical composition but also partially on their molecular mass. However the copolymer separation presented in Fig. 2 is mainly carried out based on chemical composition differences even if copolymer molecular mass is not very high (<20 000). Indeed, the highest-molecular-mass copolymer (based on EO_{12} units) elutes the first because it has the highest polarity.

The peak shape of copolymer with grafted $(EO)_4$ units differs from the other copolymer peaks; this copolymer is also the only one that gelled after several weeks, whereas the others were stable for months.

Fig. 3 presents the chromatographic separation of a polyglycol branched copolymer in comparison with a polyglycol end-blocked copolymer. Both copolymers have a similar degree of polymerisation (DP = 150 for PDMS) and are coupled with the same polyglycol homopolymer (CH_2=CH$(EO)_{12}$OH). The more polar copolymer (graft copolymer with ten polyglycol units per silicone chain) elutes earlier than the block copolymer (two polyglycol units per PDMS backbone).

3.3. Chromatographic separation on a silica column

The second option for the separation of polyglycol–silicone copolymers is to precipitate residual polyglycols and the copolymer in trimethylpentane (TMP) and operate the elution by increasing the amount of a more polar solvent, like THF. Using a CN column and starting with a non-polar alkane solvent, like trimethylpentane, low-molecular-mass

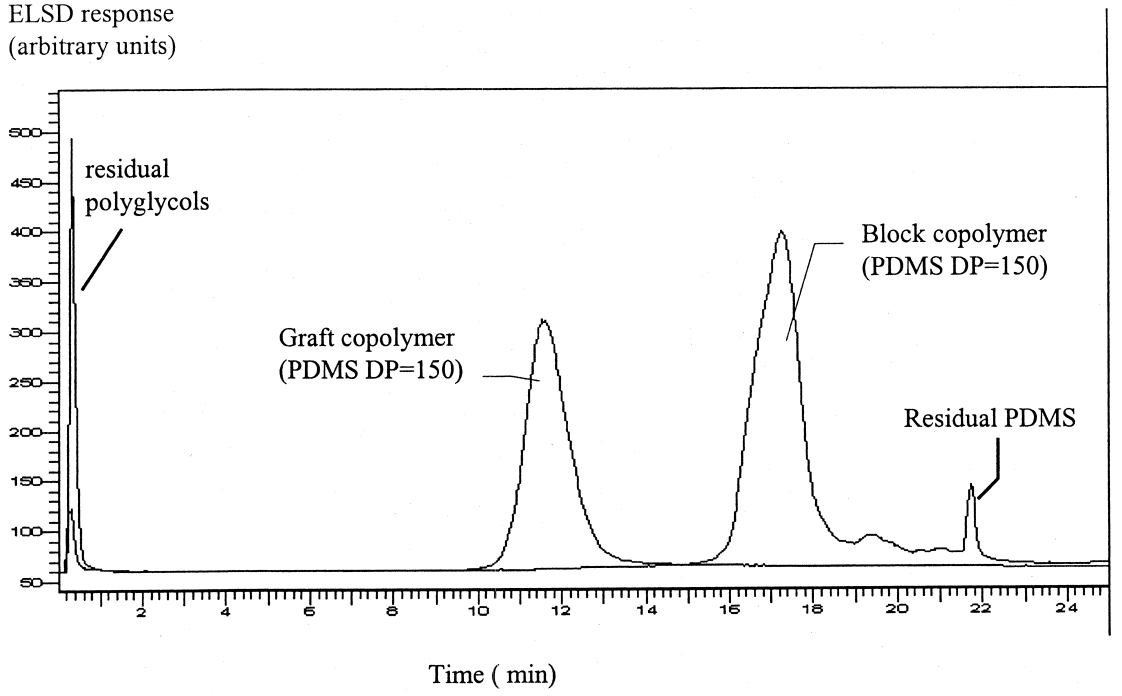

Fig. 3. Gradient chromatograms of polyglycol branched copolymer and polyglycol end-blocked copolymer. Gradient from 100% water to 100% isopropanol. Nova-Pak CN guard column.

copolymers and polyglycol homopolymer do not precipitate on the column. This phenomenon is called breakthrough. In this case, the precipitation process is not instantaneous and take a certain time, the polymer and copolymer then elute in the dead volume of the CN column without precipitation.

To avoid breakthrough problems, we decided to induce some polar interactions between polar polymers and the stationary phase and to use a polar stationary phase, like silica guard column. Due to the affinity of the stationary phase for polar groups, the precipitation of polyglycol homopolymer and the copolymer is induced by elution of the non-solvent.

The retention process for copolymer samples in TMP–THF solvent system on silica column relies on initial precipitation of the copolymer and residual polyglycols followed by redissolution in the solvent gradient. In order to facilitate the desorption of polar molecules on the stationary phase, 20% methanol is added in THF as a hydrogen bond displacer. Without methanol in the eluent, peaks are broad and flat due to H-bond interactions with the stationary phase. Using these conditions, the PDMS homopolymer elutes in the dead volume.

Fig. 4 shows HPLC separation of a block copolymer sample on silica column. The first peak is assigned to residual PDMS homopolymer which is soluble in TMP. The second peak is assigned to the block copolymer which is well resolved from polyglycol hompolymer (i.e. the third peak).

Fig. 5 shows the influence of the degree of polymerisation (DP) of the PDMS backbone on the copolymer retention time for block copolymers. As expected, the copolymer retention time decreases when the degree of polymerisation of PDMS increases. The chromatogram shows that the retention time of the copolymer with a low PDMS DP (i.e. DP = 25, M_r = 2100 g/mol) nearly matches the re-

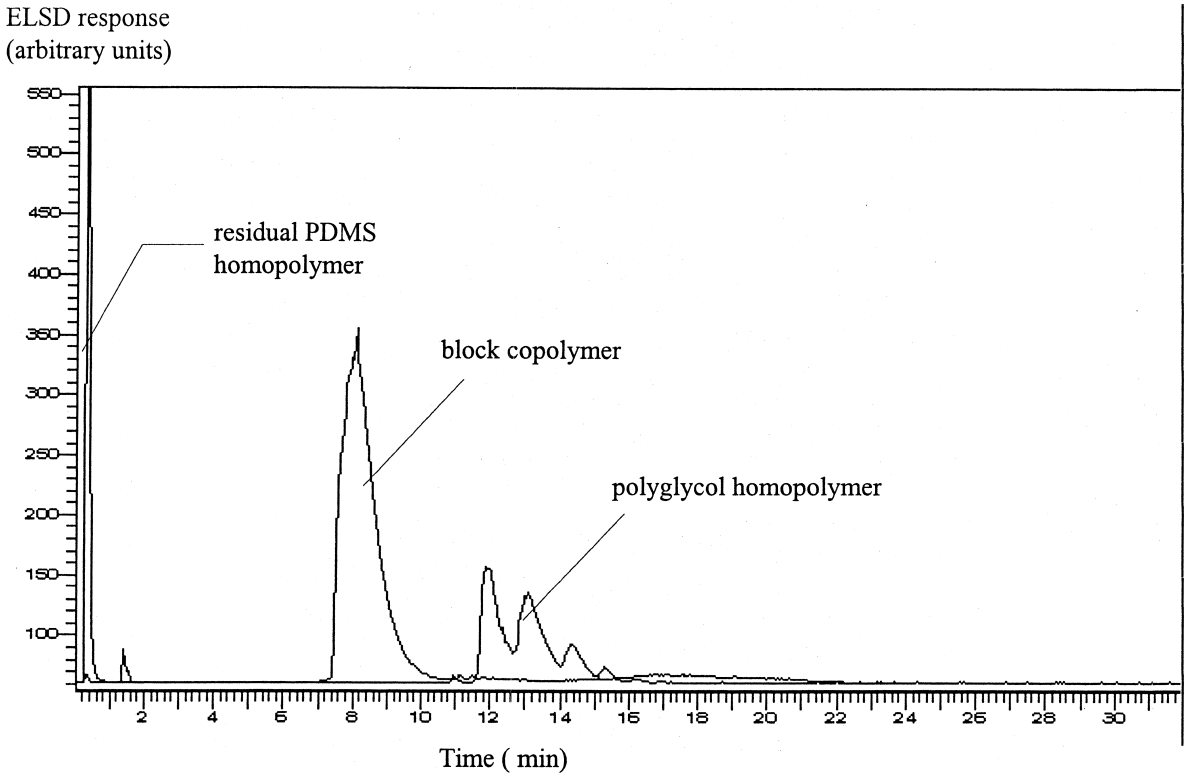

Fig. 4. Gradient chromatograms of block copolymer sample and polyglycol homopolymer on silica guard column. Gradient from 100% TMP to THF–methanol (80:20).

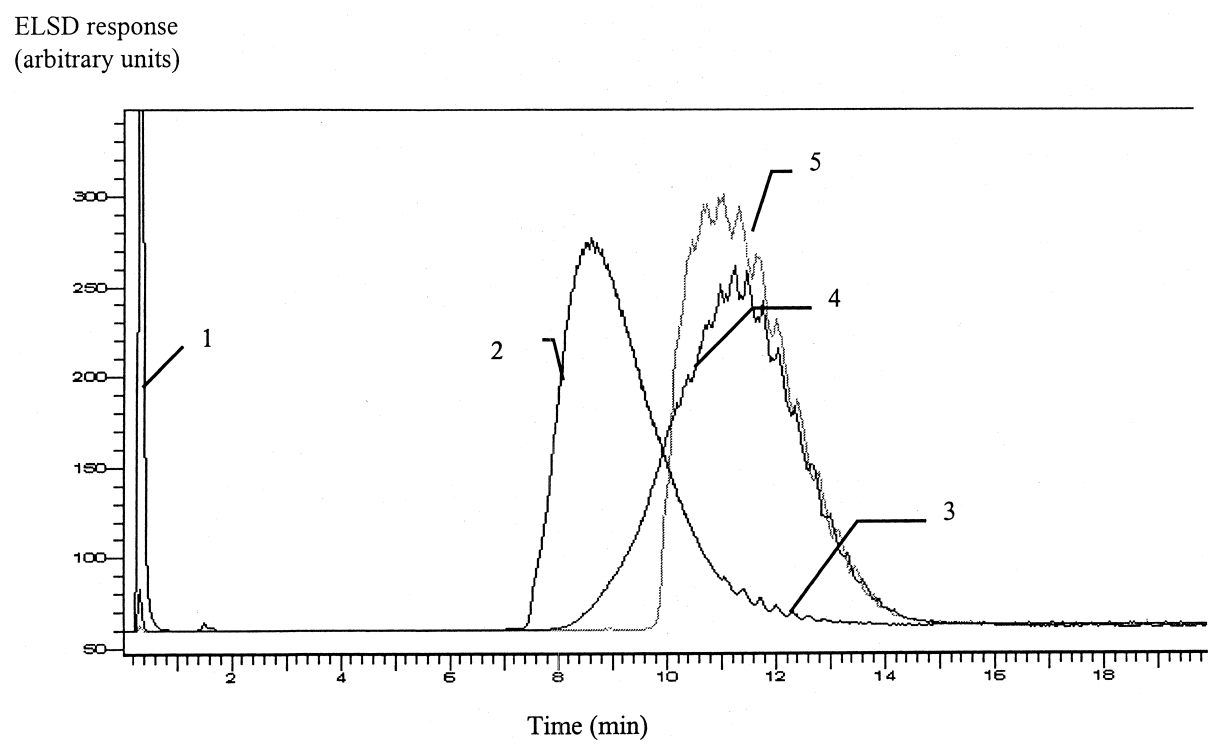

Fig. 5. Gradient chromatograms of polyglycol M500, block copolymers at DP 25 and 150. 1=Residual PDMS, 2=block copolymer of DP=150, 3=residual polyglycol, 4=block copolymer of DP=25+unreacted polyglycol, 5=polyglycol homopolymer. Gradient 100% TMP to THF–CH_3OH (80:20). Nova-Pak silica guard column.

tention time of unreacted polyglycol homopolymer. In the case of a copolymer with a high PDMS DP (i.e. DP=150, M_r=11 900 g/mol), the chromatogram shows a better separation between the copolymer and unreacted polyglycol homopolymer.

The retention time (t_R) of the copolymer is generally located between the retention times of the starting homopolymers. Fig. 4 shows that block copolymer is located between the starting silicone and the polyglycol. On the other hand, Fig. 6 shows that graft copolymer elutes after the starting polyglycol. This can be explained since graft copolymers are obtained from a PDMS polymer of DP 100 with 10 mol% Si–H groups; this means that ten polyglycol units are covalently linked to the PDMS backbone thereby increasing artificially their glycol molecular mass leading to a lower solubility in low polarity solvents. Furthermore, analyses are carried out on silica columns which will interact strongly with the glycol moieties.

4. Conclusion

GPEC coupled to ELSD is perfectly adapted to the analysis of organosilicone copolymers. It enables the separation and quantification of unreacted homopolymers in a coupling reaction between two polymers and the characterization of the copolymer based on its chemical composition distribution. In the use of low-molecular-mass copolymers, the gradient separation is a factor of their chemical composition and their molecular masses. The use of short HPLC column (i.e. guard column) to carry out their separation leads to bad resolution and broadening of individual polymer peaks. Although interactions with the column are usually avoided when running GPEC, the use of ‘real’ high resolution HPLC column may be indicated for low- and medium-molecular-mass copolymers in order to reduce peak broadening and increase resolution. Future work with these HPLC columns is planned.

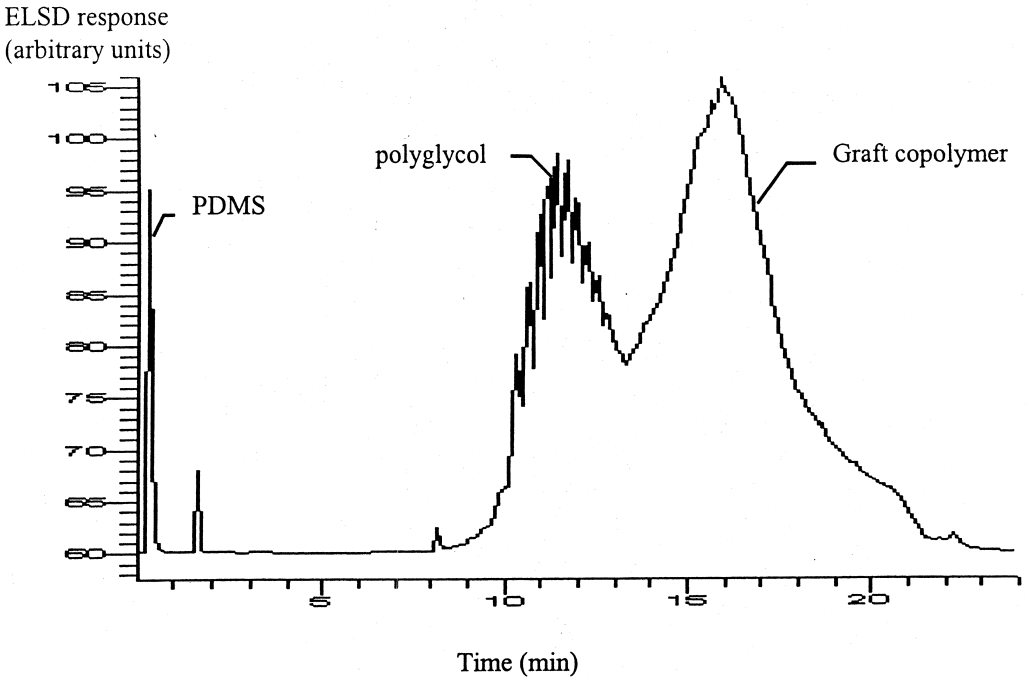

Fig. 6. Gradient chromatogram of a graft copolymer sample. Gradient from TMP to THF–methanol. Nova-Pak silica guard column.

The technique has also been used for the characterization of other organosilicone copolymers, such as PMMA–PDMS copolymers and silicone–urethane copolymers. New developments are currently being carried out with an Alliance HPLC system (Waters).

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