

CHARACTERISATION OF TELECHELIC AND COPOLYMERS BY LIQUID CHROMATOGRAPHY TECHNIQUES

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Introduction

By combining species with differing chemical properties, telechelic polymers and block copolymers can be synthesised which display novel phase behaviour and surfactant properties with wide-ranging industrial applications. Recent advances in polymer chemistry have made production of many new materials of this type synthetically undemanding. However, analysing the molecular structure of these materials is not trivial and has often employed expensive and time-consuming techniques such as NMR. This paper discusses the application of liquid chromatography techniques to the analysis of telechelic polymers and block copolymers, which can be used to probe the molecular composition of materials with relatively simple and inexpensive equipment.

Method development for this type of separation is very much application dependent. For example, in the case of gradient polymer elution chromatography (GPEC) and critical point chromatography (LCCC), the choice of sorbent, solvents and gradient will depend upon the chemistry of the polymer to be analysed. In addition, the application of gradient elution and the limited optical properties of synthetic polymers usually dictate that the preferred detection method for this type of analysis is evaporative light scattering detection (ELSD). This presentation will illustrate the effectiveness of such LC techniques in the elucidation of polymer composition for a number of case studies.

The chromatographic systems used in the work presented in this poster comprised of a PL LC-1150 4 channel gradient pump running in isocratic or gradient mode (Polymer Laboratories, UK), a Rheodyne 7125 valve (Rheodyne Corporation, USA) a PLRP-S 5µm 100Å (150x4.6mm) reverse-phase polymeric HPLC column and a PL-ELS 1000 evaporative light scattering detector (both Polymer Laboratories, UK).

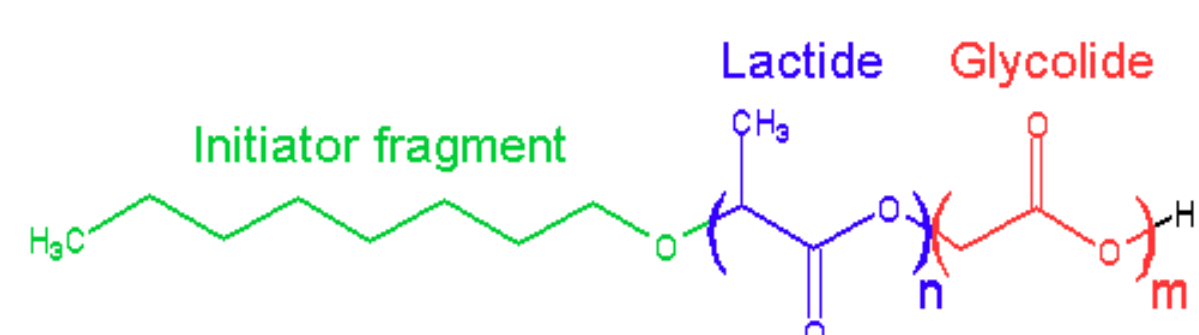
Gradient Polymer Elution Chromatography (GPEC)

Gradient polymer elution chromatography (GPEC) is a general term used to describe the chromatographic analysis of polymers applying an eluent gradient. Typically the term is used to describe the compositional separations of copolymers using columns packed with reverse or normal phase porous HPLC media. The GPEC experiment is carried out with standard HPLC equipment with a detector that is insensitive to the gradient – most copolymers do not contain chromophores and so ultra-violet / visible detectors are of limited use and evaporative light scattering is the most common form of detection.

To obtain a separation based on the composition of a copolymer as opposed to a separation in interactive (i.e. HPLC) mode, careful selection of the eluents must be made. In the GPEC experiment a gradient is applied which moves from a poor solvent for the copolymer to a good solvent. When the sample is injected into the system the poor solvent conditions result in phase separation and precipitation of the copolymer. The gradient progresses and the strength of the solvent increases until good solvent conditions are reached and the precipitated polymer re-dissolves. Once in solution the copolymer can also interact with the porous column media. If the column interaction is dominated by a size exclusion mechanism, the copolymer will migrate down the column faster than the solvent front. As the polymer elutes down the column it, leaves the region of good solvation and migrates into an area of poor solvent conditions, re-precipitation occurs and the copolymer remains undissolved until the solvent strength increases and the good solvent conditions are re-established. This redissolution / reprecipitation process will occur many times down the column length until elution from the column is achieved. Under these conditions, elution of the copolymer will be controlled by the relative solubility of the components of the copolymer in the good and bad solvents and so a separation based on the composition of the copolymer can be obtained.

GPEC is an excellent technique for analysing materials with a chemical composition distribution (CCD) such as copolymers as the following case studies illustrate.

GPEC Analysis of Random Poly(lactide-co-glycolide) (PLGA)



Poly(lactide-co-glycolide) is a commercial polymer with applications in the medical industry due to its biodegradation properties. It is a random copolymer of lactide and glycolide monomers both of which have similar structural units and solvation properties. For the GPEC experiment, an eluent conditions consisting of a 2 minute hold in 99% methanol followed by linear gradient of 1-99% THF in ten minutes was employed. The results of the GPEC experiment are shown in figures 1 and 2. The results show that:

- The retention time of the copolymer was found to be independent of the molecular weight (Mn)
- The retention time of the copolymer showed a linear correlation with % glycolide in the polymer backbone
- The separation of the copolymers of different compositions was controlled by the relative solubility of the monomers units in the two solvents

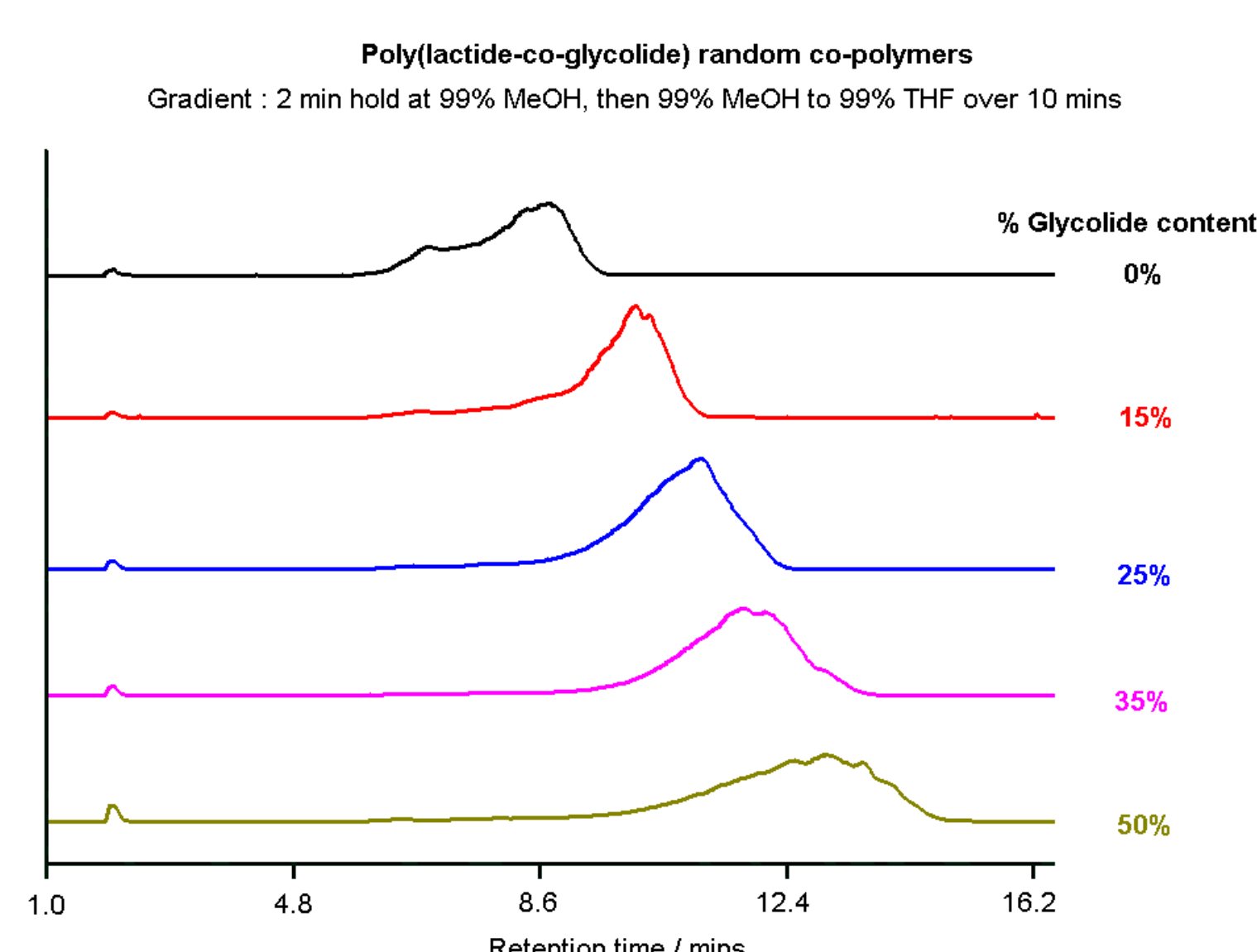


Figure 1: Chromatograms of a series of poly(lactide-co-glycolide) polymers by GPEC

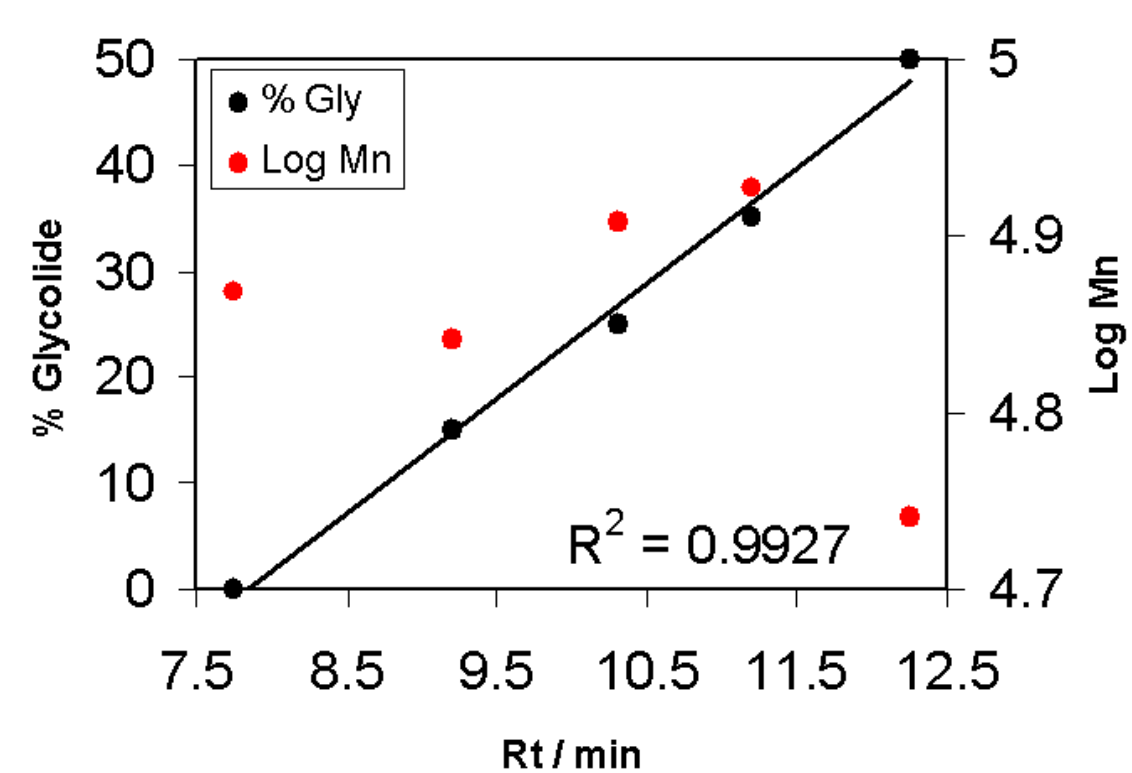
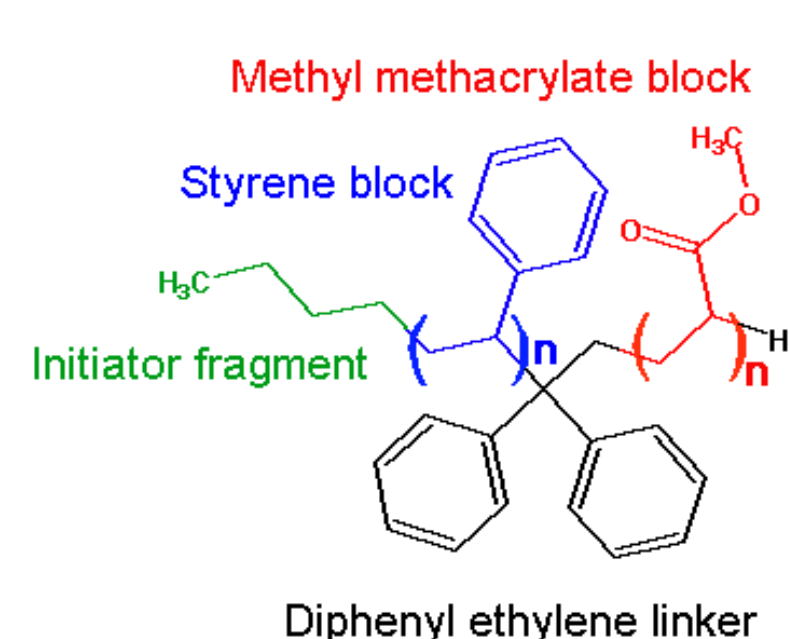


Figure 2: Plot of the correlation between retention time and molecular weight and % glycolide content for a series of poly(lactide-co-glycolide) copolymers analysed by GPEC.

GPEC Analysis of Block Poly(styrene-*b*-methyl methacrylate)



Copolymers of styrene and methyl methacrylate can be produced by the sequential addition of monomers to a living cationic polymerisation. The two monomers have widely differing polarities leading to two blocks of differing solution behavior. These polymers are described as amphiphilic and have unusual phase behavior and surfactant properties. For the GPEC experiment, eluent conditions consisting of a 2 minute hold in 80% methanol followed by linear gradient of 20-100% THF in ten minutes were employed. The results of the GPEC experiment are shown in figures 3 and 4. The results show that:

- The the retention time of the copolymer was found to be independent of the molecular weight (Mn)
- The retention time of the copolymer showed a correlation with % styrene in the polymer backbone
- The non-linear correlation was observed which is typical of block copolymers

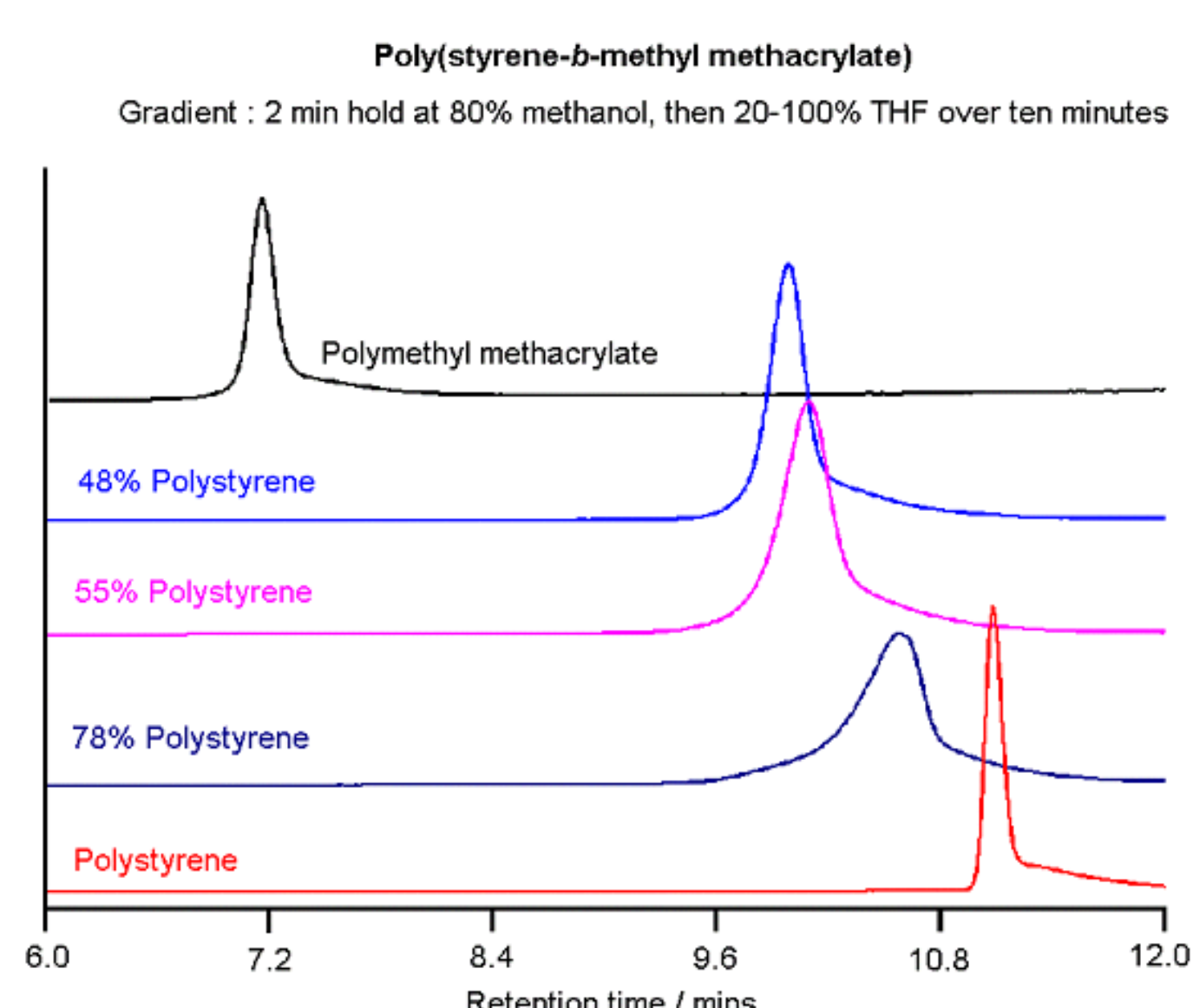


Figure 3: Chromatograms of a series of poly(styrene-*b*-methyl methacrylate) polymers by GPEC

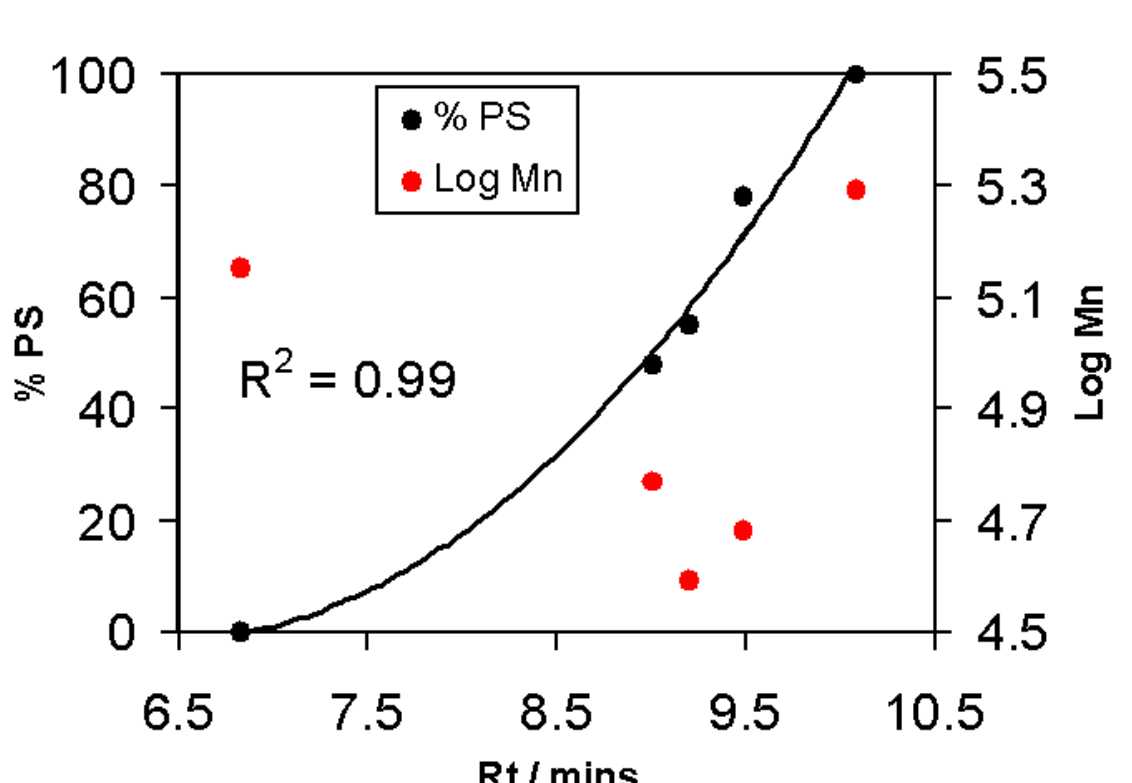


Figure 4: Plot of the correlation between retention time and molecular weight and % styrene content for a series of poly(styrene-*b*-methyl methacrylate) copolymers analysed by GPEC

Critical Point Chromatography

In liquid chromatography, polymer samples are introduced into an eluent flowing through a column packed with porous media (typically polymeric or silica beads). Any retention between the polymer and the column media results from a reduction in the free energy of the polymer in solution:

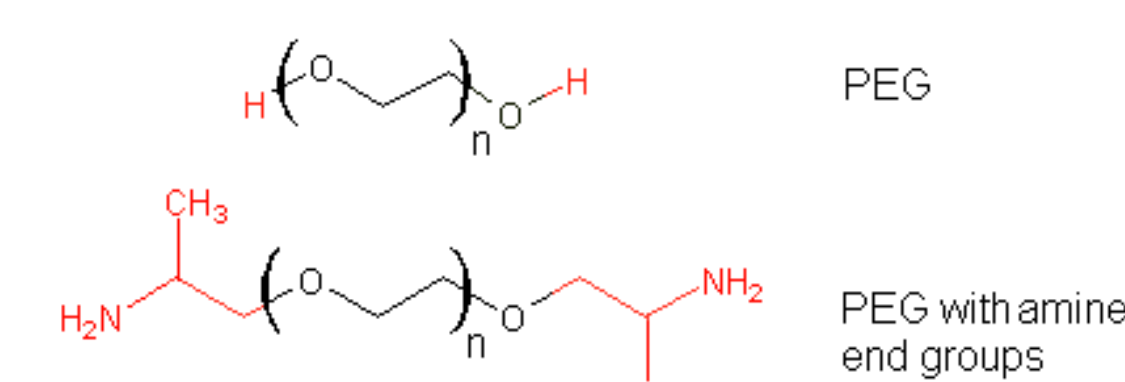
$$\Delta G = \Delta H - T \Delta S$$

If reverse/normal phase absorption occurs then ΔG is negative because ΔH will be negative, if a size exclusion mechanism occurs then ΔG will be negative because ΔS is positive. Separation of individual components of the polymer occurs if the reduction in ΔG differs between the components. For many polymers altering the choice of chromatographic eluent will with a particular choice of column determine whether the retention mechanism is primarily or exclusively interaction or size exclusion. Critical point conditions exist where ΔH and ΔS are balanced for a given polymer/solvent combination and there is no change in ΔG during the separation. Under these conditions the polymer will elute at the total permeation limit of the column regardless of the molecular weight of the sample. At the critical point the polymer is said to be 'chromatographically invisible' as no separation is obtained. For the majority of polymers the critical point can be determined by making the appropriate selection of column, temperature and eluent.

Critical point chromatography is very useful for obtaining compositional information for polymers with a functional type distribution (FTD) such as polymer with differing end groups or containing comonomers. If critical conditions are applied for one component of a sample, that component becomes chromatographically invisible and any separation observed is controlled by other components, such as different end groups or comonomers in the sample. Critical point chromatography is carried out under isocratic conditions and therefore can be performed on a standard liquid chromatography equipment.

Telechelic Polyethylene glycol (PEG)

Critical point chromatography can be used to study telechelic polymers which contain end group functionality. If critical conditions for the main backbone of the polymer are employed, then separation occurs only based on the end group functionality. Critical point chromatography was employed to analyse a telechelic polyethylene glycol containing amine end groups.



Critical conditions were established for PEG by analysing a series of PEG narrow standards isocratically with varying solvent compositions, as shown in figure 5. The following critical point conditions were found for the PEG backbone:

Column: PLRP-S 5µm 100Å (150x4.6mm)
 Eluent: 49% acetonitrile (ACN) in water
 Flow Rate: 1.0 ml/min
 Inj Vol: 20µl
 Detector: PL-ELS 1000 (Nebuliser : 70°C Evaporator : 80°C Gas flow : 1.0 SLM)

Above 49% acetonitrile in the eluent size exclusion occurred, below 49% acetonitrile interactive reverse-phase chromatography took place. However, at the critical point elution was independent of molecular weight. The telechelic PEG with amine end groups was then analysed under the critical conditions for PEG. A second sample of the telechelic PEG was analysed after neutralisation of the amine groups with hydrochloric acid to form the HCl salt. Figure 5 shows the chromatograms obtained.

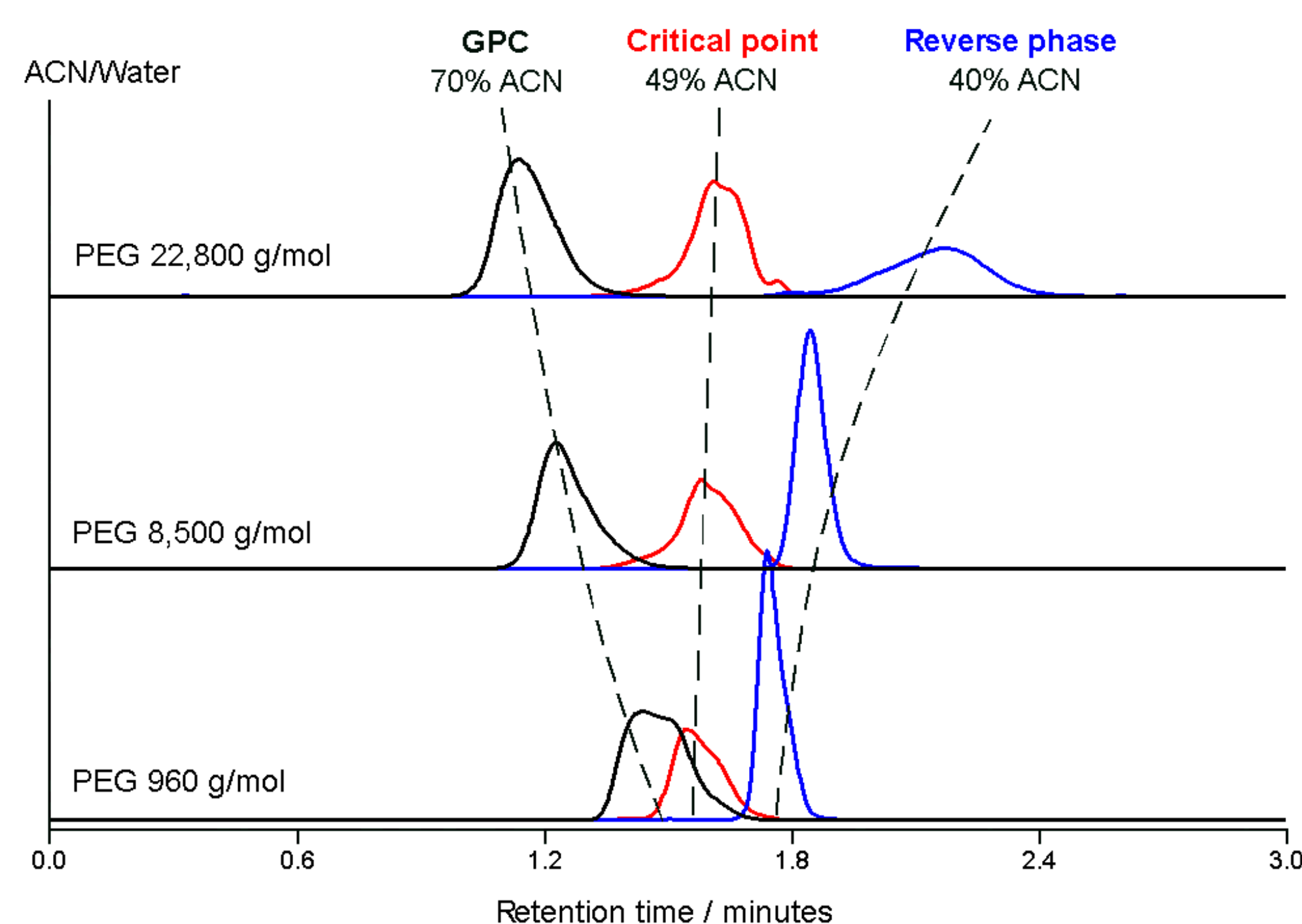


Figure 5: Establishing critical conditions for PEG.

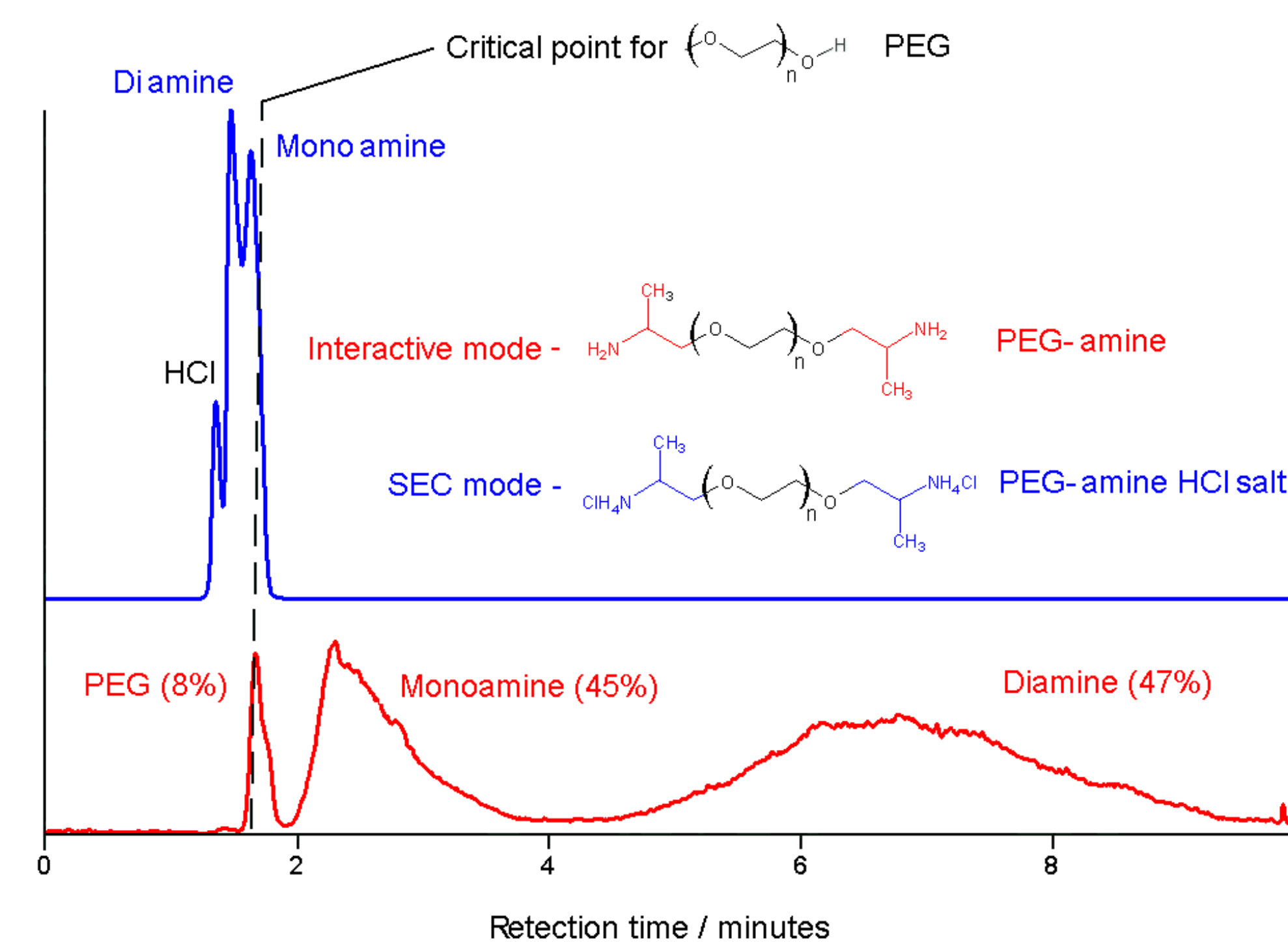


Figure 6: Chromatograms of the PEG with amine end groups before and after neutralisation with HCl under PEG critical conditions.

Under the critical conditions for PEG, it was found that the amine end groups on the telechelic PEG interacted with the column by a reverse phase mechanism, allowing the PEG chains with one and two amine groups to be resolved. Neutralising the amine with HCl greatly increased the polarity of the end groups such that the separation mechanism switched to size exclusion.

Summary

Gradient polymer elution chromatography and critical point chromatography are two relatively new developments in liquid chromatography that can be applied to the analysis of polymers. Using conventional liquid chromatography equipment, information about the structure of copolymers and the presence of modified end-groups can be determined. However, a drawback of these technique is that the analysis conditions must be determined individually for each application.