

Critical retention behavior of homopolymers

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CRITICAL RETENTION BEHAVIOR OF HOMOPOLYMERS

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ABSTRACT

The isocratic retention behaviour of a homopolymer at a specific temperature and varying solvent compositions can be divided into three modes: exclusion mode, transition mode (critical conditions) and adsorption mode. Under critical conditions (a specific non-solvent/solvent composition at a specific temperature) the retention of a homopolymer is independent of the molar mass. The critical conditions depend upon the temperature, the type of polymer and the type of non-solvent/solvent mixture. A difference in the critical conditions between polystyrene standards and polybutadiene standards was found. No significant influence of different types of column packing on the critical solvent composition was noticed. The exact mechanism of the retention of a polymer under critical condition is not clear yet.

In order to determine the critical conditions, a new method has been developed. The method can be easily performed on existing equipment. The method contains a different setup of the data acquired by isocratic HPLC than methods described in literature. Therefore, less experiments need to be performed to determine the critical conditions compared to the current method. The newly developed method is more efficient than the methods described in the literature.

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INTRODUCTION

The interest in the separation of polymers by liquid chromatography has grown during the last decade. New high performance liquid chromatography (HPLC) methods have been developed to characterize polymers.

In order to obtain the chemical composition of a polymer the HPLC method gradient polymer elution chromatography (GPEC[®]) can be used. Methods resembling GPEC[®] have been described in literature as high performance precipitation liquid chromatography HPPLC [1] or liquid adsorption chromatography [2]. The separation of polymers by GPEC[®] is based on the differences in solubility of polymers. The molar mass distribution (MMD) of a polymer can be determined by the isocratic HPLC method size exclusion chromatography (SEC).

The isocratic retention behaviour of a homopolymer can be divided into three different modes: an exclusion mode, a transition mode and an adsorption mode. The isocratic retention behaviour of a homopolymer depends on the solvent conditions at a specific temperature. By changing the non-solvent/solvent composition at a constant temperature the three retention modes can be observed.

In the exclusion mode a strong solvent is used. Therefore no interaction between the column packing and the polymer occurs. The polymer molecules move through the column and are excluded from the pores of the column packing. As can be seen in figure 1(A), the retention increases with decreasing molar mass of the polymer molecules.

By increasing the volume percentage of non-solvent (vol% NS) at a specific temperature the solvent strength decreases. The retention mode changes from exclusion mode to the adsorption mode. At high %NS the

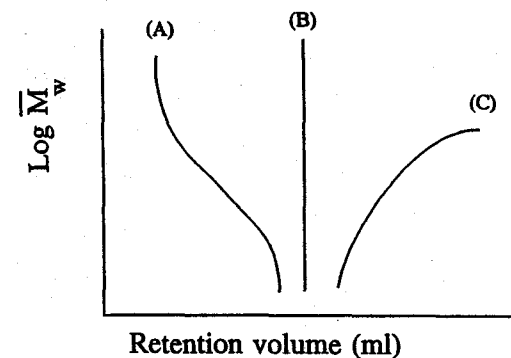


FIGURE 1

Plot of $\log \bar{M}_w$ Versus Retention Volume (ml) at Different Vol% NS; (A) %NS < CSC, (B) %NS is CSC and (C) %NS > CSC.

solvent strength is so low that interaction between the column packing and the polymer molecules occurs. As a result the sequence of retention in adsorption mode is proportional to the increase of the molar mass of the polymer molecules (see figure 1(C)).

In between the two modes a transition mode exists. If the polymers differ in molar mass but not in chemical structure a non-solvent/solvent composition is reached at which the polymer molecules elute simultaneously. The combination of the non-solvent/solvent composition and the particular temperature is called the critical conditions [3] and the composition is referred to as the critical solvent composition (CSC).

The CSC depends upon the temperature, the non-solvent/solvent mixture and the type of polymer. At the CSC, the separation is independent of the molar mass of the polymer molecules (see figure 1(B)).

Gorshkov *et al.* [3-7] have studied the critical retention behaviour and the influence of the temperature on the critical conditions of a solvent/column system. The same authors have also described the three isocratic retention modes in thermodynamic terms.

The isocratic HPLC method performed at the critical conditions is called critical polymer chromatography (CPC). Polymers which only differ in functionality or end-groups can be separated by CPC [3-7]. Additionally, polymers which differ in topology (*e.g.* grafted, linear) can be separated under critical conditions [8,9].

A method to determine the critical solvent conditions at a specific temperature is described by Gorshkov *et al.* [3-7]. Many experiments are necessary to obtain the critical conditions of a specific system (column, solvents, polymer). The retention volume of polymer standards at different non-solvent/solvent compositions at a constant temperature are obtained. The molar mass of each polymer standard is plotted versus the retention volume of the polymer standards at a certain non-solvent composition. The curves of the molar mass of the polymer versus the retention volume at different non-solvent/solvent compositions can be plotted in one figure (see figure 1). Under critical conditions the retention volume is independent of the molar mass. Therefore, the slope of the critical curve becomes infinite.

In order to determine the critical conditions using the method according to Gorshkov *et al.* [3-7], many experiments are needed and therefore the method is time consuming. In order to reduce the time and number of experiments a new simple method of determining the critical conditions will be introduced.

EXPERIMENTAL

Materials

Equipment : the equipment consisted of a Waters 600E gradient controller and pump, a Waters U6K variable loop injector and a column oven.

Two detectors were used: the Waters 484 variable wavelength ultra violet absorbance (UV) detector (254 nm) and the ACS 750/14 mass detector. The mass detector is an evaporative light-scattering detector [10] and was used to detect polybutadiene (polybutadiene has no significant UV absorbance). The eluent flow was established at 0.5 ml/min.

Columns : the used columns were Deltapak C18 100 Å (pore size= 100 Å, $d_p = 5 \mu\text{m}$, 3.9x150 mm, Waters Part No. 11795), Deltapak C18 300 Å (pore size= 300 Å, $d_p = 5 \mu\text{m}$, 3.9x150 mm, Waters Part No. 11793), Novapak C18 (pore size= 60 Å, $d_p = 4 \mu\text{m}$, 3.9x300 mm, Waters Part No. 11695), μ Styragel HT (pore size= linear, $d_p = 10 \mu\text{m}$, 7.8x300 mm, Waters Part No. 3554). The column temperature was (in all experiments) 30°C.

Solvents : the used solvents were tetrahydrofurane (THF) Westburg HPLC grade (not stabilized) and water of the Milli-Q water system of Millipore. During the experiments Helium was sparging the solvents.

Polymer samples : the polymers used in the experiments were polystyrene standards of TSK (\bar{M}_w : 500, 3000, 5600 and 9100 g/mol). The polybutadiene standards are from Polymer Labs (\bar{M}_w : 900, 3000, 8000 and 9300 g/mol). It is important that the standards used for each experiment have the same functionalities, because under critical conditions the adsorption of the functional group effects the retention. In order to guarantee the same end-group of each standard type the standards used for one experiment had to be of the same company. The concentration of the polymer solutions in THF was 0.1% (g/l). The injected volume of the sample was 25 μl .

Methods

The retention volumes of the different polymer standards were obtained isocratically at different volume %NS, starting with 100% solvent at constant

temperature. By increasing the non-solvent composition the retention volume increases. The retention volume of each polymer standard can be plotted versus the non-solvent composition.

The curves (k' versus non-solvent composition) of all polymer standards can be plotted in one figure (see figure 2). This figure is called the CSC plot. The intersection point relates to the non-solvent composition at which the polymer standards with the same chemical structure but with different molar mass elute simultaneously. The critical conditions or the critical solvent composition (CSC) can be defined by this particular non-solvent composition and the specific temperature.

RESULTS AND DISCUSSION

Method to determine the critical conditions

Few experiments are necessary to determine the critical conditions in contrast to the method of Gorshkov *et al.* [3-7]. The retention volumes of the polymer standards of the same chemical type but with different molar mass are obtained at different non-solvent/solvent compositions at a specific temperature. In the figures 2 and 3 the retention volume (V_R) is replaced by a coefficient k' which is defined as $(V_R - V_0)/V_0$. V_0 is the zero retention volume of the system.

The accuracy of the determination is about $\pm 1\%$ NS. The exact critical solvent composition is defined more accurately than within 1%. Especially near the critical solvent composition, small variations in the %NS have great influence on the retention behaviour. Since the solvent composition can not be established more accurately than 1%, the exact critical solvent composition can be obtained by fine tuning of the temperature.

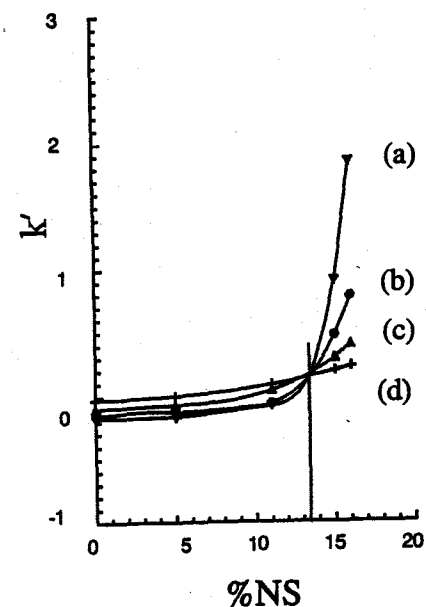


FIGURE 2

CSC Curve of Polystyrene in the Solvent System Water/THF on a Novapak C18 Column at 30°C and a Flow Rate of 0.5 ml/min; Detection: UV 254 nm; Polystyrene Standards: (a) $\bar{M}_w=9100$, (b) $\bar{M}_w=5570$, (c) $\bar{M}_w=2980$ and (d) $\bar{M}_w=500$ g/mol.

In order to compare the method described in literature and the introduced method, the acquired data (figure 2) are presented in figure 4 according to the technique developed by Gorshkov *et al.* [3-7]. The curves show the relation between the molar mass and the retention volume at certain %NS. As can be seen in figure 4 the critical solvent composition cannot be determined. No curve is obtained with infinite slope. More specific experiments have to be performed when using the method of Gorshkov *et al.* [3-7].

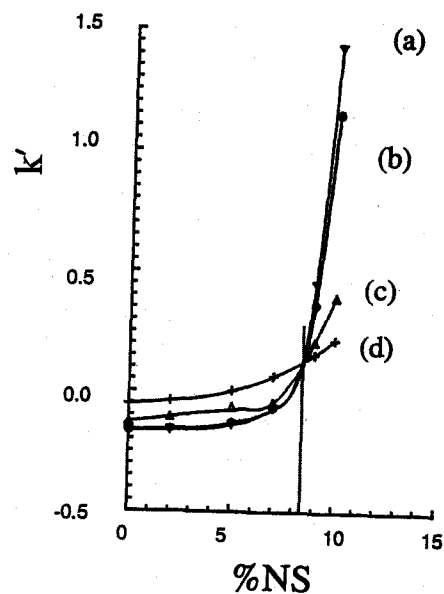


FIGURE 3

CSC Curve of Polybutadiene in the Solvent System Water/THF on a Novapak C18 Column at 30°C and a Flow Rate of 0.5 ml/min; Detection: Mass Detector; Polybutadiene Standards: (a) $\bar{M}_w=9300$, (b) $\bar{M}_w=8000$, (c) $\bar{M}_w=3000$ and (d) $\bar{M}_w=900$ g/mol.

Polystyrene

The CSC plot of the polystyrene standards is shown in figure 2. The used column is the Novapak C18 (4.0x300 mm). The increase of the flow in the range from 0.5 - 1.0 ml/min had no influence on the critical solvent composition. The critical solvent compositions determined for water/THF systems using different types of column packing were determined (see Table 1). With respect to the pore size distribution and the type column packing similar critical solvent compositions were obtained.

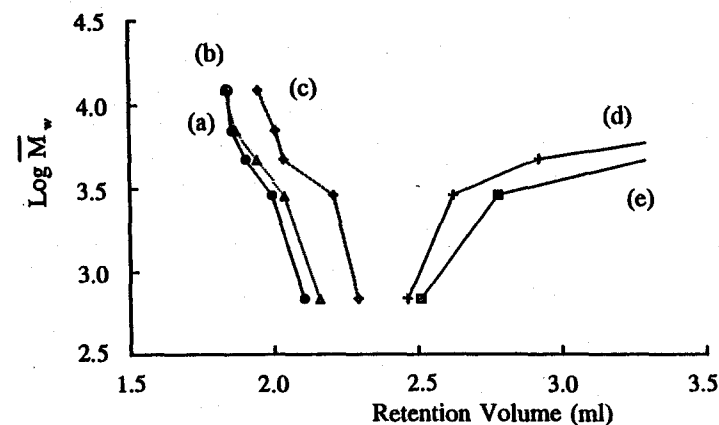


FIGURE 4

Log \bar{M}_w Versus the Retention Volume of Polystyrene Standards at Different Vol% NS ; (a) %NS=0, (b) %NS=5, (c) %NS=11, (d) %NS=15 and (e) %NS=16; Solvent System Water/THF at 35°C on a Novapak C18 Column; Detection: UV 254 nm; Polystyrene Standards: $\bar{M}_w=9100$, $\bar{M}_w=5570$, $\bar{M}_w=2980$ and $\bar{M}_w=500$ g/mol.

TABLE 1

Critical Solvent Composition (CSC) of Polystyrene Standards in the Solvent Mixture Water/THF at 30°C and Different Types of Columns.

Column	CSC (%water)
Novapak C18	13
μ Styragel HT	11
Deltapak C18 (100Å)	11
Deltapak C18 (300Å)	12

Polybutadiene

In order to determine the influence of the chemical composition of the polymer on the critical solvent composition, polybutadiene was studied. The critical solvent composition in the system water/THF, Novapak C18 of polybutadiene (see figure 3) was determined. The CSC of polybutadiene appeared to be different from the CSC of polystyrene in the system water/THF, Novapak C18. The CSC of polybutadiene is 8% water and the CSC of polystyrene is 13% water.

CONCLUSIONS

The new method is accurate in determining the critical conditions at a certain temperature. By presenting the results as in the figures 2 and 3 the transition from exclusion mode to adsorption mode can easily be noticed. The newly introduced method is more efficient as compared with the existing method.

The critical solvent composition depends on the following parameters: the temperature, the type of polymer, and the solvent/non-solvent mixture. The exact contribution of each parameter in respect to the mechanism of critical polymer chromatography is still unclear. Especially the role of the temperature is not completely understood. Moreover, the theory of adsorption of polymer molecules does not satisfactorily describe the critical retention behaviour.

Additionally no significant differences in the critical solvent composition occur when different types of column packing are used. This implies that the adsorption of a polymer molecule is more dependent on the polymer type than on the type of column packing.