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Retention behaviour of polystyrene oligomers in reversed-phase liquid chromatography

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Abstract

Reversed-phase liquid chromatography (RPLC) was employed to investigate the behaviour of low-molecular-mass polystyrene oligomers with three different end groups, *n*-butyl, *sec*-butyl, and *tert*-butyl polystyrenes. Exothermodynamic retention studies on the polystyrene oligomers were carried out using a C₁₈ stationary phase column and 100% methanol mobile phase over the temperature range 15 to 60 °C. The resulting van't Hoff plots were linear over the entire temperature range for all three end group polystyrenes. Enthalpy–entropy compensation (EEC) showed a linear compensation for the higher-order oligomers, but was non-linear for the lower-order oligomers, indicating a change in the mechanism of retention. Differences in the extent of retention for each of the three end groups were also apparent. The ramifications of these differences are discussed.

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1. Introduction

Studies on the behaviour of homologues in reversed-phase liquid chromatography (RPLC) very often reveal information about elution mechanisms. For the most part, retention in a reversed-phase system is considered to be dominated by solvent–solute interactions, with the stationary phase playing a passive role, acting essentially as a solute receptor [1]. On reversed-phase surfaces modified with alkyl chain moieties (such as C₁₈, C₈ and C₄) the relationship between log *k* (where *k* is the retention factor) and the number of carbon atoms in the homologous

series (*n_c*) depends on the nature of the homologous series and the type of column employed [1–3]. For instance, the homologous series of alkyl benzenes display an incremental increase in retention as the alkyl chain length increases [1–3]. By studying the exothermodynamic behaviour of solute members of the homologous series, changes in the retention mechanism according to the ligand surface can be evaluated [1–6]. The lower members of the homologous series most often elute according to a partitioning process, whilst for the higher members of the series the mechanism is observed to change to adsorption or quasi-partitioning–adsorption, depending upon the chain density and the organic modifier concentration [7]. On a C₁₈ column, the change in mechanism for alkyl benzene homologues occurs when the number of carbon atoms in the homologous

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member is between 14 and 15 [3]. This is referred to as the critical carbon number [2,3]. As the alkyl chain length of the modified silica surface decreases the critical carbon number also decreases. For a C_8 column, the critical carbon number is between 8 and 11 [2] with between four and eight carbon atoms for a C_6 stationary phase.

While alkyl benzenes give useful insights into retention processes in RPLC, their behaviour may not necessarily be used to gauge the retention behaviour of an oligomeric series of low-molecular-mass polystyrenes. The polystyrene oligomers contain bulky side groups, which may modify the retention behaviour, both from a steric aspect and also from a solvent interaction aspect. Furthermore, the oligomer end group may affect the retention process, being either bulky and branched, or a long-chain linear hydrocarbon.

The retention of oligomers, such as oligostyrenes, in reversed-phase liquid chromatography has been studied for several decades [8–14]. The separation of the oligostyrenes has been well documented, to the extent that even the conditions that determine diastereoisomer resolution have been well defined [12–14]. Exothermodynamic studies of low-molecular-mass polystyrenes by Philipsen et al. [8] revealed that, like alkyl benzenes, oligostyrenes are also susceptible to changes in the retention mechanism depending on the degree of polymerisation. According to the study by Philipsen and coworkers, when the degree of polymerisation exceeded 13 monomer units, enthalpy–entropy compensation graphs revealed a change in the elution mechanism. The authors claimed this to be a change from adsorption to partitioning, although the oligomer chain length in terms of actual carbon numbers (irrespective of the phenyl ring) far exceeded the critical carbon number as predicted by studies using alkyl benzenes [8]. Philipsen et al. tentatively suggested that the change in retention was due to a bending of the polymer chain, allowing “multi-site” partitioning to occur. As this was a tentative assessment of the retention behaviour, further studies are required before this type of “multi-site” partitioning can be considered to be an accurate interpretation of the retention phenomena.

While size-exclusion chromatography relies essentially on the steric exclusion of the polymer from a

porous network as the mechanism behind the separation process, retention and separation in reversed-phase methods are determined by chemical factors [15–20]. In general, reversed-phase methods yield oligomeric separations with greater resolution than conventional size-exclusion methods. Such separations allow molecular mass determinations to be carried out using the adsorptive or partitioning processes of RPLC. Further enhancement of the resolution in RPLC may be gained using solvent gradient elution [15,17–19,21–23] or thermal gradient elution [24,25] techniques. The partitioning or adsorptive-type interactions that are responsible for the molecular mass separations in oligomeric series also allow for interactions to occur between the polymer end group and the stationary phase surface, as shown in the works by Lee et al. [25] and Jandera and coworkers [26,27]. In these studies important changes in selectivity were apparent between polymers with the same structural repeating unit, but with significant differences in the end group, such as changes in the polarity or bulky nature of the end group. End group selectivity may also be apparent for polymers eluting under “critical conditions”, where exclusion effects and adsorptive interactions exactly compensate [27]. In the present study we show further details on how a subtle change in the branching of the polymer end group affects the retention process. In this study, the end group of the polymer is changed from *n*-butyl to either *sec*-butyl or *tert*-butyl. This subtle change in end group may go unnoticed when calibration standards are purchased and, as a result, lead to calibration errors. In addition, one of the primary aims of this study is to illustrate the change in retention behaviour of the oligomeric series as a function of the degree of polymerisation, defining the transition from partitioning to adsorption.

2. Experimental

2.1. Chemicals

HPLC-grade methanol and dichloromethane were obtained from Mallinckrodt Australia. Tetrahydrofuran was obtained from Sigma–Aldrich. Polystyrene standards with molecular masses of 580 (*n*-

butyl) and 760 (*sec*-butyl) Daltons were purchased from Polymer Laboratories and Aldrich, respectively. *tert*-Butyl polystyrene (molecular mass ~580 Daltons) was synthesised using anionic polymerisation of styrene initiated with *tert*-butyl lithium. The molecular masses of the members of the oligomer series were determined using mass spectroscopy [28].

2.2. Equipment

All chromatographic separations were performed on a Shimadzu LC system, incorporating a LC-10ATvp pumping system, SIL-10ADvp auto injector, SPD-10Avp UV detector (set at 262 nm), and Shimadzu Class-VP software on a Pentium II 266 MHz processor. The temperature of the column and all pre-column tubing (including a 2 mL loop prior to the injection valve) was thermostated in a water bath (± 0.2 °C). The chromatography column used in this study was a Nucleosil C₁₈ column (10 μ m P_d, 10 nm pore diameter, 100×4.6 mm) packed in-house, using methods previously described [28].

2.3. Chromatographic separations

The polystyrene standards (*n*-butyl, *sec*-butyl, and *tert*-butyl) were dissolved in dichloromethane, and made up to concentrations of approximately 10 mg/mL. All separations were conducted using a 100% methanol mobile phase, at a flow-rate of 1.0 mL/min (injection volumes were 5 μ L). Experiments were randomised, and duplicates were performed for each injection. The column temperature was deemed to be equilibrated when duplicate injections (performed 30 min apart) showed no variation in retention.

2.4. Calculation of retention factor

The determination of the time corresponding to the elution of an unretained species (t_0) is a contentious issue [29–33], and one in which there is still no clear consensus on the type of marker that should be employed. However, it is generally accepted in the chromatographic analysis of polymers that the exclusion volume of the polymer eluting under the conditions of a strong mobile phase should be used as a marker for the unretained elution volume.

Consequently, the void time used for the calculation of retention factors in the present study was determined by injection of the individual oligomer fractions (isolated using a preparative reversed-phase column [28]) into the chromatographic system using tetrahydrofuran as the thermodynamically strong solvent. All exclusion volumes of each molecular mass oligomer fraction (V_{sec}) were measured at a flow-rate of 0.5 mL/min for each of the temperatures for which reversed-phase behaviour was studied. Hence the retention factor may be given by [16]

$$k = \frac{(V_r - V_{\text{sec}})}{V_{\text{sec}}} \quad (1)$$

where V_{sec} is the elution volume of the relevant oligomeric fraction in the tetrahydrofuran SEC system and V_r is the elution volume of the same oligomer fraction in the reversed-phase separation. Furthermore, the exclusion volume of the polymer was temperature dependent, necessitating the measurement of the exclusion volume at each temperature employed in this study. The ramifications of a temperature-dependent exclusion volume with respect to the phase ratio of the system will be discussed later in the text. Suffice to say at this point, over the temperature range studied in this work, a variation in V_{sec} in the order of 6% is apparent for the $n=3$ oligomer and around 5% for the $n=11$ oligomer (see Fig. 1). If V_{sec} were measured at only a single temperature the retention factor for the early-eluting fractions would be in error by as much as 12% for some temperatures.

3. Results and discussion

There are numerous examples of oligomeric separations of polystyrenes using reversed-phase methods in the literature. Such separations can be readily achieved using a standard C₁₈ column with a mobile phase such as methanol. The polydisperse low-molecular-mass polymer sample readily fractionates into oligomeric components with elution time increasing monotonically with the molecular mass. A plot of $\log k$ versus the degree of polymerisation yields a linear calibration curve, as shown in Fig. 2. The three curves illustrated represent the calibration

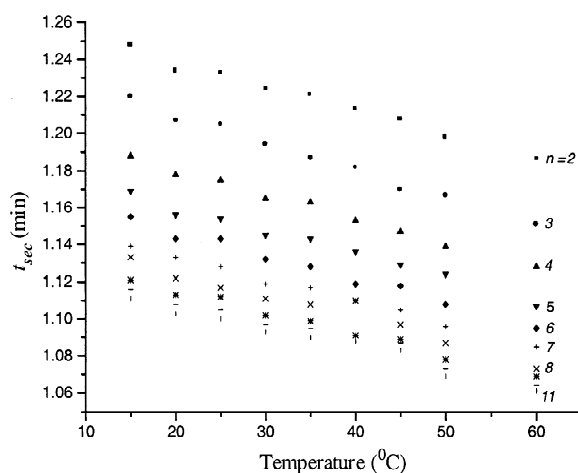


Fig. 1. Plot of t_{sec} versus temperature ($^{\circ}\text{C}$) for the *sec*-butyl end group. Mobile phase, 100% THF; flow-rate, 0.5 mL/min; Nucleosil C_{18} column; 5 μL injection volume; detection, 262 nm.

curves for the (a) *n*-butyl, (b) *sec*-butyl and (c) *tert*-butyl oligostyrenes. From these calibration curves, the molecular mass and molecular mass distribution of an unknown polymer sample can be determined [19].

However, from Fig. 2 it is apparent that errors in molecular mass determinations would be introduced if the end group of the polymer sample were not considered. For instance, the difference in elution volume between the *n*-butyl and *tert*-butyl

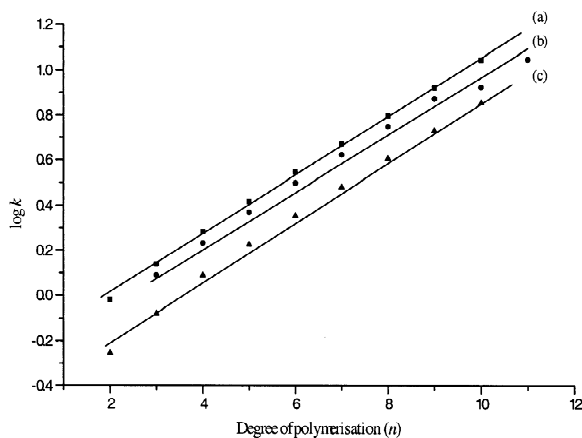


Fig. 2. Calibration curve of $\log k$ versus degree of polymerisation (n) for (a) *n*-butyl, (b) *sec*-butyl, (c) *tert*-butyl polystyrene (at 20 $^{\circ}\text{C}$). Mobile phase, 100% methanol; standard concentration, 10 mg/mL; flow-rate, 1.0 mL/min. Other conditions as in Fig. 1.

oligostyrenes with a degree of polymerisation equal to 10 was almost 4.5 mL. This amounts to a difference in the polymer chain length of 1.5 styrene units. A smaller, yet still significant, difference was observed when comparing the *n*-butyl oligostyrenes to the *sec*-butyl oligostyrenes. The end group contribution still had a significant influence on the retention behaviour as the molecular mass increased, even though it had a decreasing significance in the overall molecular structure for the longer oligomers.

Exothermodynamic relationships are frequently used to investigate the role of structural factors in chemical equilibria and rate processes [4–6]. In liquid chromatography, enthalpy–entropy compensation (EEC) relationships are used to determine the relationship between the enthalpy and entropy changes associated with solute binding. In a chromatographic sense, van't Hoff plots have long been employed to evaluate the EEC of solutes at the surface of a stationary phase support. The retention of a solute (k) is related to the enthalpy and entropy changes of a system by the well-known relationship given by [4]

$$\ln k = -\frac{\Delta H_x^0}{RT} + \frac{\Delta S_x^0}{R} + \ln \Phi \quad (2)$$

where ΔH_x^0 is the change in enthalpy and x denotes the structural variable under investigation, which in this case is the degree of polymerisation for each of the polystyrenes distinguishable by their end groups, ΔS_x^0 is the change in entropy of the system, T is the absolute temperature and R is the universal gas constant. The quantity $\ln \Phi$ is the phase ratio of the chromatographic column, which in Eq. (2) is assumed to be a constant.

The plots in Fig. 3 illustrate typical van't Hoff plots for polystyrenes eluting under the conditions described in this experiment (shown are the van't Hoff plots for the *n*-butyl polystyrenes). The van't Hoff plots were linear with correlation coefficients greater than 0.992 in all cases and for the most part greater than 0.996. Values of ΔH_x^0 derived from these plots are given in Table 1 and are shown graphically as a function of the degree of polymerisation in Fig. 4. As the molecular mass of each of the three end-group polystyrenes increased there was a linear exothermic increase (ΔH_x^0 becomes more negative)

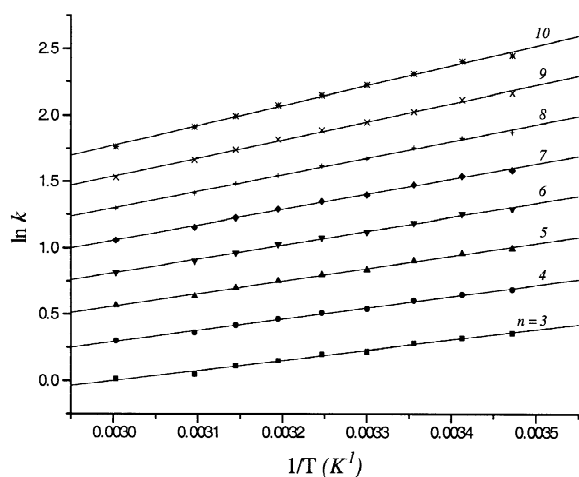


Fig. 3. Van't Hoff plots [$\ln k$ versus $1/T$ (K^{-1})] for the n -butyl polystyrenes undergoing retention on the C_{18} column in a 100% methanol mobile phase.

in enthalpic interactions associated with the solute undergoing binding onto the stationary phase. We can then write

$$\Delta H_x^0 = n(\Delta\Delta H_{xs}^0) + \Delta H_e^0 \quad (3)$$

where n is the degree of polymerisation, $\Delta\Delta H_{xs}^0$ is the slope of the plot of ΔH_x^0 versus the degree of polymerisation and represents the enthalpic interactions associated with each styrene unit, and ΔH_e^0 is the change in enthalpy associated with the end group—derived from the intercept of the linear plot of ΔH_x^0 versus the degree of polymerisation. The slopes of ΔH_x^0 as a function of the number of repeating units were 0.864 kJ/mol ($\pm 1.7\%$) for the

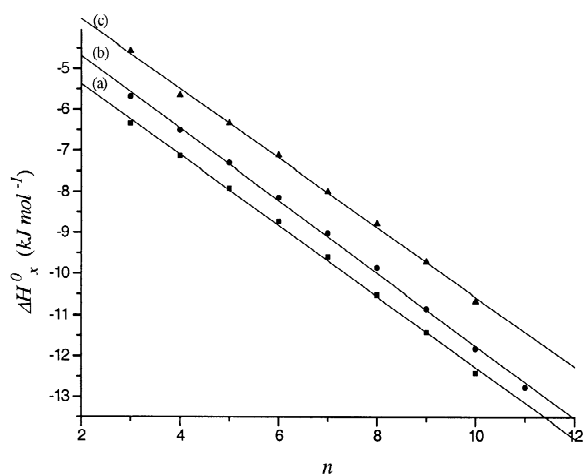


Fig. 4. Plot of the change in enthalpy (ΔH_x^0) as a function of the degree of polymerisation (n) for (a) n -butyl, (b) sec -butyl, (c) $tert$ -butyl polystyrenes.

n -butyl, 0.886 kJ/mol ($\pm 1.5\%$) for the sec -butyl and 0.848 kJ/mol ($\pm 1.8\%$) for the $tert$ -butyl end group polystyrenes. These are equivalent within the experimental precision. The enthalpic contribution of a styrene repeat unit was obtained as an average of these values (0.87 kJ/mol). The enthalpic contribution (ΔH_e^0) associated with the respective end groups was equal to -3.64 kJ/mol ($\pm 3\%$) for n -butyl, -2.91 kJ/mol ($\pm 3\%$) for sec -butyl and -2.10 kJ/mol ($\pm 5\%$) for $tert$ -butyl polystyrenes. The enthalpic interactions associated with the end groups were three to four times greater than the values associated with each styrene unit. So, while the addition of a styrene repeat unit amounted to a change in enthalpy of 0.87 kJ/mol for each of the

Table 1
Enthalpy data derived from the slopes of the van't Hoff plots illustrated in Fig. 2

Degree of polymerisation	ΔH_x^0 (kJ/mol)		
	n -Butyl	sec -Butyl	$tert$ -Butyl
3	-6.33 ± 0.24	-5.69 ± 0.26	-4.56 ± 0.28
4	-7.13 ± 0.17	-6.51 ± 0.20	-5.65 ± 0.17
5	-7.92 ± 0.19	-7.31 ± 0.23	-6.34 ± 0.19
6	-8.73 ± 0.20	-8.14 ± 0.21	-7.13 ± 0.17
7	-9.59 ± 0.18	-9.02 ± 0.20	-8.00 ± 0.13
8	-10.51 ± 0.22	-9.87 ± 0.22	-8.78 ± 0.16
9	-11.42 ± 0.25	-10.85 ± 0.25	-9.71 ± 0.18
10	-12.41 ± 0.29	-11.83 ± 0.26	-10.66 ± 0.19
11		-12.77 ± 0.30	

polystyrenes, the relative change in enthalpy between the three different end groups was more substantial. The difference in the enthalpic interactions between polystyrenes with an *n*-butyl end group and a *tert*-butyl end groups was 1.58 kJ/mol. This is equivalent to almost two styrene units. The difference in enthalpic interactions between the *n*-butyl and *sec*-butyl oligostyrenes was less significant, being 0.61 kJ/mol, which is slightly less than the equivalence of a single styrene unit. Clearly, the steric hindrance of the end group is significant in the retention process.

Eq. (2) reveals that the change in entropy of the system associated with solute binding can be determined from the intercept of the linear van't Hoff plot. However, this assumes that the phase ratio of the column is known, which requires knowledge of the mobile phase column volume and the ligand surface coverage on the stationary phase support. In the present study, all experiments were conducted on exactly the same column. All experiments were run over a 5-day period during which temperatures and polymer injections were randomised. Comparisons were made between each of the three different end-group oligostyrenes in this system only, and consequently the phase ratio and its contribution to the change in entropy should have remained constant in the time-frame of the study. However, as we have seen, V_{sec} is a function of both temperature and molecular mass, or, more precisely, the molecular size or hydrodynamic volume of the polymer. Since V_{sec} is temperature dependent, either the phase ratio varies and cannot be assumed to be constant or there are variations in the molecular size or hydrodynamic volume of the oligomers at these different temperatures. A change in the hydrodynamic volume of the polymer would manifest itself in a change in the "apparent" phase ratio. Nevertheless, the relationship between V_{sec} and temperature is linear, as shown in Fig. 1, and consequently we assume that if the "apparent" phase ratio does in fact vary with temperature then this variation is systematic. As one of our primary aims in this study was to illustrate the end-group contribution to retention and its subsequent effect on molecular mass determinations we recorded all chromatographic retention data under identical conditions on the same column. As a result, our reported values of ΔS_x^0 contain a contribution from the phase ratio. The plots in Fig. 5 illustrate the

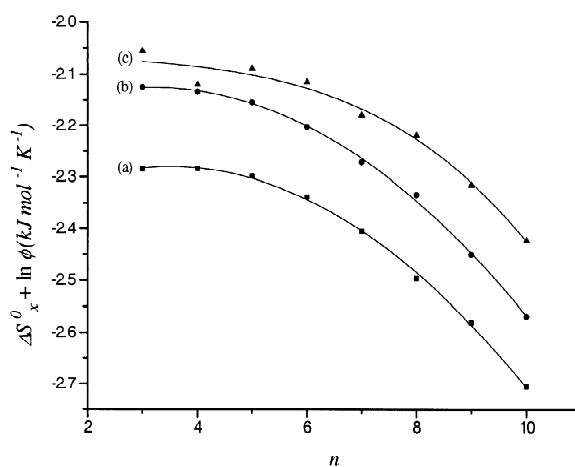


Fig. 5. Plot of the change in entropy ($\Delta S_x^0 + \ln \phi$) as a function of the degree of polymerisation (n) for (a) *n*-butyl, (b) *sec*-butyl, (c) *tert*-butyl polystyrenes.

change in entropy as a function of the number of configurational repeating units for each of the three different end group oligostyrenes. In each curve, the change in entropy becomes increasingly negative as the molecular mass increases, corresponding to a greater change in order following solute binding. However, this relationship is not linear with respect to molecular mass. This non-linearity is not due to the potentially variable "apparent" phase ratio as the departure from linearity is substantially greater than the contribution that may be associated with a realistic variation in the phase ratio. For instance, if we assume a phase ratio in the order of 0.18 [8] in accordance with the calculations from Philipson et al., the curvature observed in Fig. 5 remains significant even if the phase ratio changes by more than 50%.

The enthalpy–entropy compensation (EEC) in this system is illustrated in Fig. 6, where the relative change in ΔH_x^0 is plotted as a function of the relative change in ΔS_x^0 . (Note: the experimental ΔS_x^0 term contains the factor associated with the phase ratio, therefore by measuring the relative change in ΔS_x^0 we obtain the entropic contribution for this particular column operating under the conditions described.) For this, we defined a reference peak (oligomer $n = 6$) and determined the relative change in the change in enthalpy ($\Delta \Delta H_x^0$) and the change in the

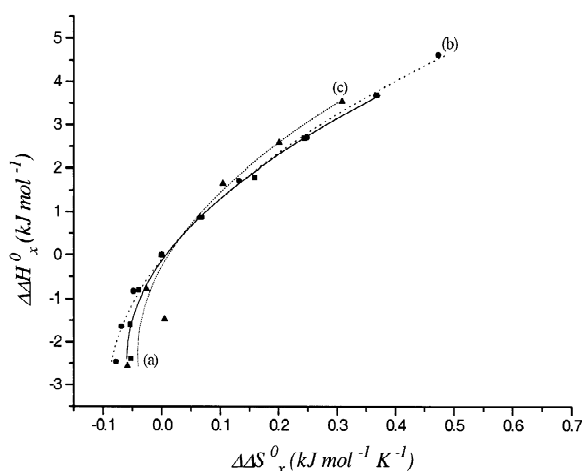


Fig. 6. Plots of the relative change in enthalpy ($\Delta\Delta H_x^0$) versus the relative change in entropy ($\Delta\Delta S_x^0$) for (a) *n*-butyl, (b) *sec*-butyl, (c) *tert*-butyl polystyrenes.

change in entropy ($\Delta\Delta S_x^0$) relative to oligomer $n = 6$. Hence some values of $\Delta\Delta H_x^0$ and $\Delta\Delta S_x^0$ are positive and others negative. Absolute magnitudes of ΔS_x^0 are not obtained using this procedure, but further comparisons may be made to other systems that have also established the relative changes in enthalpy and entropy as a function of the degree of polymerisation or the contribution of end groups. The EEC plots of each of the three oligostyrenes are almost coincident, although there are minor differences in their rates of curvature. These differences are below the precision limits of the experimental measurements and in any case suggest only minor differences between the retention processes for each of the sets of oligostyrenes. Perfect linear compensation is only observed for oligomers with more than six to eight configurational repeating units. For oligomers with fewer configurational repeating units, the slope of the curve continually changes, indicating that a change in the retention mechanism is occurring. This is related to the size of the polymer, but almost independent of the end group.

Support for the change in mechanism as molecular mass increases may be found in the relationship between selectivity and the degree of polymerisation, n , as shown in Fig. 7 for the *n*-butyl polystyrenes. In this figure, selectivity is plotted as a function of the degree of polymerisation over the range of tempera-

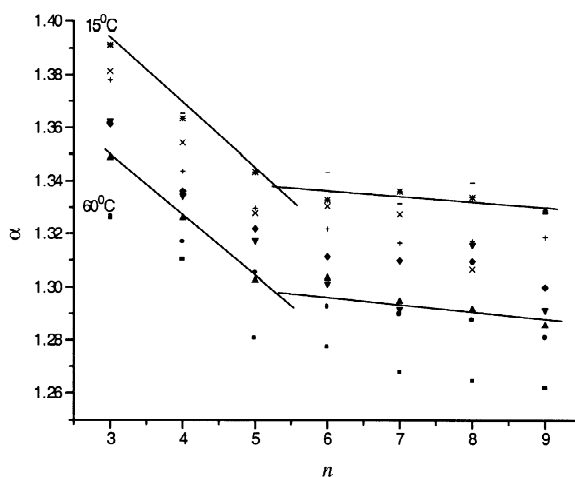


Fig. 7. Plots of the selectivity (α) as a function of the degree of polymerisation (n) for the *n*-butyl polystyrenes undergoing retention on the C_{18} column in a 100% methanol mobile phase at temperature between 15 and 60 °C.

ture studied. Two regions of linearity are observed in each of the plots shown in Fig. 7, irrespective of the end group or temperature. These plots are very similar to those of Tchapla et al. [2,3] except that, in their studies, which employed a number of homologous series, three regions of linearity were apparent. The three linear regions corresponded to (i) partitioning for the low members of the homologous series, (ii) quasi-partitioning–adsorption processes as the carbon number in the homologous series approached the critical carbon number and (iii) adsorption for the higher members of the homologous series. In the present work we speculate that the two regions represent quasi-partitioning–adsorption processes for the $n=3$ to $n=5$ (or 6) oligomers and predominantly adsorption processes for oligomers greater than $n=6$. The region corresponding to partitioning-dominated retention might have been observed had we tested lower members of the series.

Non-linearity in the relationship between ΔS_x^0 and molecular mass (as shown in Fig. 5) has also been observed by Philipsen and coworkers in a study on the retention behaviour of low-molecular-mass polystyrenes using a tetrahydrofuran–water mobile phase and a C_{18} stationary phase [8]. The non-linearity observed by Philipsen et al., however, was less significant than that presented in the current study

and occurred more predominantly at higher molecular masses—in the order of $n=13$, above the limits of this study. Philipsen and coworkers were somewhat surprised that such a curvature may be a result of a change in retention mechanism from partitioning to adsorption, given that the bulky nature of the polymer would to some extent limit partitioning effects. They instead speculated that the longer polymer chains may bend sufficiently to enable both ends of the polymer chain to be inserted into the C_{18} layer in a partitioning fashion. In the current study, the transition between the two different retention mechanisms occurred around oligomer $n=5$ (for *n*-butyl polystyrene—see Fig. 6), which is much too small to undergo sufficient bending to enable insertion of both ends into the C_{18} layer. However, the significance of this transition from quasi-partitioning–adsorption to predominantly adsorption occurring at the $n=5$ to 6 oligomer is that a polymer main chain of this length contains from 14 to 16 carbon atoms, including the four carbon atoms of the *n*-butyl end group. This coincides almost perfectly with the critical carbon number (equal to 14 or 15) for alkyl benzene homologues undergoing partitioning on C_{18} surfaces [2]. Perhaps the difference in the results observed by Philipsen and coworkers and the present study is related to the different solvent environments and the behaviour of the stationary phase in these environments. One could perhaps imagine that the C_{18} alkyl chains may be more extended from the surface in the enriched tetrahydrofuran environment, which may open additional avenues for partitioning-type interactions. The apparent relationship between the critical carbon number ($n=5$ to 6 oligomer) and the transition from a quasi-partitioning mechanism to a predominantly adsorption mechanism may be fortuitous, but the experimental data presented in this work support this change in mechanism. This is surprising for two reasons: (a) the bulky nature of these types of molecules should make penetration into the stationary phase surface difficult, in much the same manner that high-density packing materials limit partitioning of smaller solutes [7], and (b) adsorptive-type interactions usually dominate at the high organic content of the mobile phase. However, Tchaplal et al. [2,3] found that the critical carbon number was constant irrespective of the type of homologous series employed and our experiments are in close agreement.

4. Conclusion

We have shown in this study that determination of molecular masses of low-molecular-mass polymers is critically dependent upon the end group of the oligomer chain. Ignorance of the end group could lead to a substantial error in the molecular mass determination. We would also speculate (and several studies illustrating selectivity of diastereoisomers confirm [12–14]) that tacticity is a determining factor in the degree of retention, although we have not yet tested this hypothesis using a thermodynamic approach. Several interesting factors have come to light through the present study. Firstly, for the oligostyrenes studied, the retention mechanism is essentially independent of the type of end group, but dependent on the molecular mass. We propose that partitioning is favoured at low molecular masses and adsorption dominates once the polymer chain length exceeds the critical carbon number. For the lower-molecular-mass oligostyrenes, entropic and enthalpic effects do not compensate proportionally. However, whether the mechanism of retention is dominated one way or the other by partitioning or adsorption is immaterial to the separation of polymers. Selectivity was greatest between oligomers separating according to a process governed by quasi-partitioning–adsorption, but selectivity decreased rapidly (1.4% per styrene unit). Once adsorption processes dominated, the selectivity decreased at a lower rate, in the order of 0.2% per styrene unit.

Secondly, while the retention mechanism is dictated to a certain degree by molecular mass but is essentially independent of the end group, the enthalpic interactions over the molecular mass range studied remained constant as a function of the degree of polymerisation. However, the exact extent of the overall enthalpic binding was dependent on the type of end group, which has important implications for the absolute retention and the establishment of calibration curves in reversed-phase systems.

We have not yet investigated the extent to which the end group remains chromatographically significant as the molecular mass increases. We would speculate that the significance should decrease as the molecular mass increases, as the end group becomes only a minor component of the overall molecular size. Continuing studies seek to investigate this effect.

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