Liquid Adsorption Chromatography of Copolymers: Molar Mass (In)dependent Retention

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ABSTRACT: Liquid adsorption chromatography with a continuous solvent gradient elution has been shown by several authors to often separate random and graft copolymers according to their chemical composition whereas their molar masses do not play an important role. A tentative explanation of this finding is presented. It is assumed that the copolymer species travel along the column with a velocity which exactly corresponds with that of the eluent composition, exhibiting a displacing power just necessary to prevent a fast progress of the macromolecules due to their exclusion. Under specific circumstances, retention of macromolecules at this adsorption promoting "barrier" depends almost exclusively on the copolymer composition and not on its molar mass. This hypothesis is based on the mechanism of the recently proposed and tested liquid chromatographic elution of homopolymers under limiting conditions of desorption and takes into account the simultaneous effect of adsorption and exclusion of macromolecules onto/from the column packing.

Introduction

The determination of mean molar masses (MMM) and molar mass distributions (MMD) of copolymers represents a very complicated analytical task. In many cases, size exclusion chromatography (SEC) is applied for this purpose. However, SEC separates macromolecules on the basis of differences in their molecular sizes which depend simultaneously on both their molar mass and chemical composition. Therefore, it is only exceptionally possible to obtain precise and reliable data on the MMM and MMD of copolymer samples by SEC alone even when applying multiple detection. Numerous attempts have been published to determine the latter characteristics of copolymers applying other analytical methods. Most of these methods are based on a separation of macromolecules exclusively or at least prevailingly according to either their molar mass or chemical composition. The resulting fractions are then subjected to further independent separation. We refer here to two-dimensional approaches to the molecular characterization of copolymers. For example, if one succeeds to separate a copolymer according to its chemical composition, the resulting fractions can be successively and independently analyzed as to their molar mass by SEC.

A promising method in this respect is liquid adsorption chromatography (LAC) (see e.g. short reviews by Teramachi,[1] Sato,[2] and Mori[3]) which is called also gradient elution polymer chromatography.[4] The latter term can be considered as a general one involving also procedures based mainly on precipitation−redissolution mechanisms.

In LAC, macromolecules are usually dissolved in an adsorption promoting solvent (an adsorli) and injected into the liquid chromatographic (LC) column packed with an active (adsorptive) material and flushed with an adsorli eluent. Injected macromolecules are adsorbed and retained at the column inlet. Subsequently, a liquid is introduced into the column in which the amount of desorption promoting liquid (a desorli) continuously increases. At a certain eluent composition, macromolecules start moving along the column, and the rate of their elution depends mainly on their composition. Several authors[1,3−9] have shown that, by using appropriate column packing and adsorli/desorli gradient, many copolymers can be efficiently fractionated according to their composition while the effect of their molar mass is small or even negligible.

In this paper, we are trying to elucidate processes that are operative within adsorption controlled LAC separation systems and to tentatively explain the molar mass independent retention in this method. To support our reasoning, we must briefly introduce a novel LC method based on a combination of exclusion and adsorption mechanisms, namely liquid chromatography of macromolecules under limiting conditions of desorption (LC LCD).[10]

In LC LCD, macromolecules are dissolved in an adsorli and injected into a column, packed with porous adsorptive material. The column is flushed with an eluent of constant composition which promotes desorption of macromolecules. Injected macromolecules are temporarily retained at the column inlet. They start moving after their initial solvent has moved away. The "limiting conditions of desorption" can be identified at which the injected macromolecules move just behind the adsorli sample solvent "barrier", irrespectively of their molar mass (cf. the scheme in Figure 1). In other words, macromolecules with different molar masses elute within the same retention volume at the limiting conditions of desorption. For a given polymer and column packing, these limiting conditions include the adsorptive strength of sample solvent and its injected volume, further the displacing strength of the eluent, temperature, and column length.

Examples of LC LCD behavior were presented in our recent paper.[10] A series of medium broad MMD poly(methyl methacrylate)s were injected in toluene adsorli into a set of two columns packed with bare silica gels. Eluents were mixtures of toluene and tetrahydrofuran (THF). The LC LCD conditions applied for eluent compositions between 50 and 60 wt % of toluene. For eluents containing higher concentration of THF desorli, the polymer elution was governed by the SEC mechanism while the adsorption mechanism of separation

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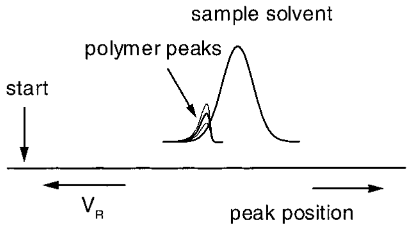

Figure 1. Schematic representation of the principle of liquid chromatography under limiting conditions of desorption. The polymer sample is dissolved in an adsorption promoting liquid and injected into a column containing porous, adsorptive packing. Eluent promotes polymer desorption. The sample solvent forms an adsorptive barrier which cannot be surmounted by macromolecules. Polymer species accumulate at the tail of the solvent zone irrespective of their molar masses and injected concentrations. Note that the sample position has an opposite orientation in comparison with the sample retention volume.

dominated if the eluent contained more than 60 wt % of toluene adsorli.[10]

One can conclude that under limiting conditions of desorption the molar mass independent elution of a homopolymer with a given adsorptivity is the result of the coupling of two mechanisms. One mechanism is the size exclusion that accelerates the progression of macromolecules along the LC column in comparison with the initial solvent zone. The movement of the solvent zone is slowed due to the accessibility of all column packing pores for small molecules. The second mechanism which is operative in the LC LCD column is the adsorptive retardation of a polymer species by the slowly moving adsorli barrier that cannot be surmounted by macromolecules. As a result, macromolecules accumulate near the tail end of the adsorli barrier independently of their molar mass or molecular size (cf. Figure 1).

It is anticipated that the LC LCD behavior would be similar for copolymers and homopolymers. The adsorptivity of a copolymer species will be dictated mainly by its chemical composition.

In LAC, the solvent gradient can be considered a continuous barrier with gradually changing retentive properties. Copolymer molecules with different compositions will “find” the appropriate positions within this continuous barrier independently of their molar mass. In other words macromolecules of different composition will accumulate at different positions of the adsorli barrier. In the systems where macromolecules accumulate at the gradient barrier practically independently of their molar masses the LAC elution will be insensitive to this parameter.

The proposed hypothesis is indirectly supported by the following experimental observations: (i) wide pore LAC column packings afforded molar mass dependent retention for smaller (nonexcluded) macromolecules of copolymers that were eluted without molar mass effects from narrow pore packings;[7,8] (ii) nonporous packings allowed practically no gradient LAC separation;[11] and (iii) elution of random copolymers depended on both the composition and the molar mass of macromolecules when the full adsorption−desorption procedure with a nonporous column packing was applied.[12]

In the above cases, the acceleration of macromolecules due to their exclusion was either diminished (i) or practically absent (ii and iii), and the progress of polymer species was exclusively governed by their adsorption. In turn, the best molar mass independent elution was attained if the LAC column was packed with a very narrow pore (3 nm) material.[8,9,13]

Our tentative explanation of molar mass independent retention in LAC of copolymers certainly possesses some weak points. For example, it is generally accepted that adsorption and desorption processes of macromolecules depend on the polymer molar masses.[14] These dependences can be easily studied by the recently developed dynamic method, especially when attaching an on-line SEC instrument to the container in which adsorption and desorption processes take place.[15,16] The conclusions resulting from both static and dynamic adsorption−desorption measurements agree well, at least qualitatively. Macromolecules with higher molar masses need a stronger displacer (e.g., more desorli in a mixture with adsorli) to initiate their desorption. This means that the elution start for copolymer molecules that were initially retained at the column inlet would depend not only on their composition but also on their molar mass. In this situation, the packing pores must be sufficiently small, and the LAC column must be adequately long to reach a dynamic balance between exclusion and adsorption of macromolecules and, consequently, their molar mass independent elution. Further, we suppose that the adsorptivity of copolymer molecules with a given overall composition does not depend on their physical structure. In other words, a copolymer behaves as a “homopolymer” with a specific composition. Such an assumption is well fulfilled for alternating copolymers, but its validity decreases with increasing sequence length in random copolymers. This probably explains why LAC elution of some copolymers has been found to depend on their molar masses, and the LAC elution of block copolymers does not lead to a reasonable separation.[17]

The experiments demonstrating molar mass independent LAC retention were done with model samples possessing both a relatively narrow molar mass and chemical composition distributions. Their mixtures were usually separated to demonstrate the LAC separation selectivity. The situation with real copolymer samples exhibiting a broad and continuous molar mass distribution and chemical composition distribution might be much more complicated, and the independence of retention on the copolymer molar mass might have to be reconfirmed.

To answer the above questions, a series of experiments including intensive optimization procedures are needed. The importance of molecular characterization of copolymers certainly deserves this effort.

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