Polymer 60 (2015) A1–A18

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Feature article

Flow induced conformational transitions of macromolecules and their effect on chromatographic separations

Alexander A. Kurganov [a], [*], Frantisek Svec [b], Anastasiia Yu Kanateva [a]

[a] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow 119991, Russia*
[b] *The Molecular Foundry, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA, USA*

ARTICLE INFO

Article history:
Received 2 August 2014
Received in revised form
20 December 2014
Accepted 6 January 2015
Available online 14 January 2015

Keywords:
Conformational transitions
Hydrodynamic chromatography
Size exclusion chromatography

ABSTRACT

The conformation of macromolecules is significantly affected, both in free flow as well as when flowing in a confined space. These effects play a major role when passing polymer molecules in solution through a porous system such as chromatographic column or membrane. Current theories take into account the conformational changes of polymer molecules caused by flow, and provide a description of the unusual behavior of macromolecules during chromatographic separation. Due to the changes in conformation, the flow can also cause degradation of polymers which have a very large molar mass.

1. Introduction

In the 1970s, two theories were developed in the field of polymer chemistry that examine the behavior of macromolecules in solutions under a flow gradient. The theory, elaborated by de Gennes [1], focused on conformational transitions within macromolecules, which were caused by shear strain resulting from flow gradients. It is known that macromolecules assume a coil conformation in a static solution, due to molecular Brownian motion. According to de Gennes [1], the shear strain caused by flow, results in deformation of the coil conformation, and the macromolecule elongates in the flow direction. The Brownian motion counteracts this process, and a certain critical shear rate is necessary to initiate the elongation of the macromolecular coil. As the critical value is reached, the solute polymer coil unwinds abruptly because of the hydrodynamic interactions. The de Gennes theory became well recognized, and became the basis for numerous modeling experiments directed at investigating the behavior of polymers in flow [2–6].

DiMarzio and Guttman developed another theory [7]. It focused on movement of the macromolecule itself in flow of a liquid. In contrast to de Gennes' theory, which dealt with single macromolecule, the DiMarzio and Guttman's model concerned behavior of a large number of macromolecules that differ in molar mass and, consequently, in coil size. According to their calculations, finite sized particles undergoing Brownian motion and flowing through a tube, have average velocities that depend on the coil size. Thus, they can be separated by the fluid flow. Larger molecules will move faster than their smaller counterparts [7]. It is interesting that DiMarzio and Guttman did not take into consideration the possible conformational transitions of polymer molecules, and the effect of these transitions on separation, although they did discuss the separation of macromolecules in flow. Since de Gennes discussed the purely theoretical case of a single isolated molecule, no separation, based on molar masses or on coil sizes, was assumed.

Passing polymers solutions through porous media including membranes and chromatographic columns is also complicated with the heterogeneity of the flow field, both in radial and longitudinal directions. Later studies of these systems produced experimental confirmation of de Gennes' theory, and demonstrated the unusual effects found while carrying out chromatographic analysis of polymers. It is surprising that theory of hydrodynamic chromatography (HDC) developed almost completely without taking into consideration de Gennes' theory of the elasticity of polymers. One of the goals of this review is to demonstrate that the combination of both de Gennes' and DiMarzio and Guttman's theories can be useful for understanding the separation process in HDC. More specifically, we intend in this article to convey the current knowledge in the field of theory of microscopic conformation transitions of polymers in solutions under flow gradients, the effect of confinement, which

---

[*] Corresponding author. Tel.: +7 495 955 4291.
E-mail address: kurganov@ips.ac.ru (A.A. Kurganov).

http://dx.doi.org/10.1016/j.polymer.2015.01.010

the macromolecules can encounter in the packed chromatography columns, on these transitions, and to demonstrate how the use of the theory enabled understanding of unusual behavior of macromolecules observed in hydrodynamic chromatography.

2. Conformational transitions of macromolecules in the free flow

Abrupt changes in the viscosity and birefringence of polymer solutions accompanied by changes in flow rate [8,9] are usually related to the transition of the macromolecule from coil to stretch conformation (Coil–Stretch transition, CS-transition) [1]. This transition occurs when the effect of shear strain on the macromolecule exceeds Brownian forces, which are responsible for coil conformation of the macromolecule in the static solution. According to the theory [1–3], this phenomenon is effective when shear strain occurring on the macromolecule $\dot{\varepsilon}$ becomes larger than critical value $\dot{\varepsilon}_C$. The latter is inversely proportional to the maximum relaxation time of the polymer chain τ:

$$\dot{\varepsilon}_C = \frac{A}{\tau} \qquad (1)$$

Here A is a constant close to 1. So the critical conditions for CS-transition apply when $\dot{\varepsilon}\tau \approx 1$. Relaxation time τ depends on a number of parameters such as solvent viscosity, the molar mass of the polymer, temperature, and polymer chain flexibility, and can be calculated using one of the equations presented in literature [10–12]:

$$\tau_{zimm} = \frac{\eta_S M^{\alpha}}{kT} \approx \frac{\eta_S R_{go}^3}{kT} = \frac{6.22\Phi_0 R_{go}^3 \eta_S}{RT} \qquad (2)$$

Here η_S is the solvent's viscosity, M is the molar mass of the polymer, T is the absolute temperature, k is the Boltzmann constant, α is the constant depending on the polymer nature and solvent quality that varies from 1.5 to 1.8, R_{go} is the radius of the gyration of the macromolecule in the static state, and the Fox-Flory parameter Φ_0. From combining Eqs. (2) and (1), it follows that the higher the molar mass, and the higher the solvent viscosity, then the lower the critical shear rate$\dot{\varepsilon}_C$. According to de Gennes [1], the conformational transition may have a character of first or second order transitions, depending on the profile of flow field (longitudinal, transverse, or more complex gradients) surrounding the macromolecule. Transitions of the first order may be accompanied by hysteresis. In this case, the transition is characterized by the existence of two stable conformations in equilibrium (double equilibrium). It is worth noting that according to Frank [13], it is difficult to create uniform flows in practice so that each macromolecule will experience a constant flow gradient. In real life, flow profile is usually characterized with heterogeneity and complexity. That is why various devices were suggested to create a defined flow field of defined type [2,13,14]. The most popular devices are those which produce longitudinal flow gradients, since de Gennes' theory predicted the abrupt CS-transition for this type of flow. The typical designs used to create longitudinal flow gradients (ensuring stretching of the molecule by the flow but without its movement) are shown in Fig. 1. The changes were usually documented by measuring the birefringence with a microscope. Use of these devices experimentally validated de Gennes' theory, while at the same time provided additional data that showed the necessity for some corrections of the theory.

Bird et al. [3,15,16] pointed out the following limitations of the de Gennes' model:

1) de Gennes used the model of restricted stretchable nonlinear elastic spring (dumb-bell model). This represents a very simplified model which does not correctly describe the movements of the polymer chain. For example, distance between spring ends is always equal to the mean value of its contour length.
2) de Gennes calculated the stretching of macromolecules in a flow that was independent of time and discussed the stretching of the polymer chain, which in fact depends on time (hysteresis).
3) de Gennes used Peterlin's assumption [17] that instantaneous spring stretching changes as a function of the mean square of stretching. Peterlin's assumption produced correct results for nonlinear elastic spring at a constant friction coefficient. However, if the friction coefficient is a function of distance between chain joints, then this assumption may result in S-shaped curves for dependence on the mean square distance between chain ends on a shear rate, which do not have any physical meaning.

To overcome these restrictions, Bird et al. [16] modeled the behavior of polymer chains in a single-axis stretching flow using a more complex model, in which the real chain is replaced with a bead-spring chain that has finite extensible nonlinear elastic springs (FENE model [18]). According to these calculations, polymer molecules undergo a conformational transition, and gradually change their conformation from coil to stretched but not in an abrupt manner as predicted by de Gennes. Authors in ref. [18] assumed four intermediate states: I – equilibrium coil; II – deformed coil; III – locally unraveled coil; and IV – stretched chain.

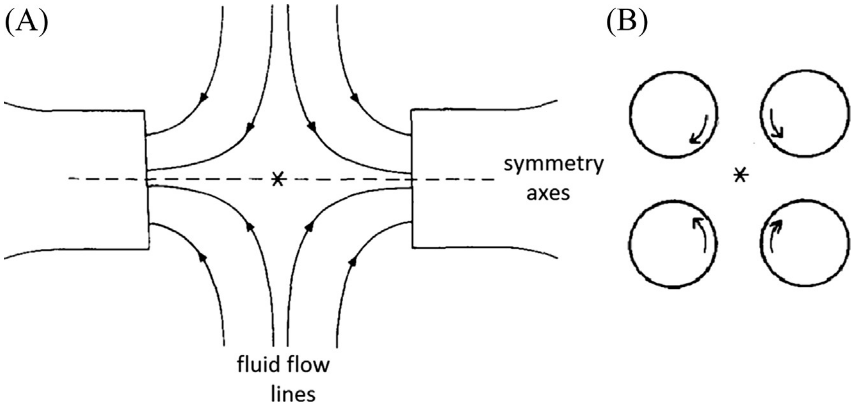

Fig. 1. Schematics of devices creating longitudinal flow gradient: (A) Device with two opposite nozzles; (B) Device including four rotating cylinders. The observation point is denoted with a cross. Reprinted with permission from Ref. [14].