

## Characterization of Polymers in Dilute Solutions

Zdenek Tuzar

Institute of Macromolecular Chemistry  
Academy of Sciences of the Czech Republic  
162 06 Prague 6, Czech Republic

### خواص البوليمرات في المحاليل المخففة

زدينك توزار

من أهم الخصائص الأساسية لمحاليل البوليمرات المستقيمة السلاسل هي معدل الوزن الجزيئي، توزيع الوزن الجزيئي، نصف قطر الدوران ونصف القطر الهيدروديناميكي.

هناك العديد من الطرق الفيزيوكيميائية لتحديد مقادير هذه الخواص منها على سبيل المثال التشتت الضوئي الثابت والمتحرك، قياس الضغط التناظري، الترسيب، كروماتوغرافيا استبعاد الحجم GPC وطريقة اللزوجة.

بالنسبة للبوليمرات المتفرعة السلاسل، يمكن تقدير درجة التفرع باستخدام عدد من الطرق المذكورة أعلاه. وفي حالة البوليمرات المشتركة والمطعمة فإن خواصاً أخرى تكون هامة جداً مثل التركيب الهندسي والبنائي والتركيب الكيميائي وعدم تجانسية هذا التركيب. في هذه الحالة فإن الطرق المهمة هي التشتت الضوئي وكروماتوغرافيا استبعاد الحجم.

إن الدقائق البوليمرية التي درست في مختبرات معهدنا لأكثر من عقدين من الزمن هي من نوع البوليمرات المشتركة المذيلة. هذه الدقائق الكروية المتعددة الجزئيات تتكون في محاليل البوليمرات الكتلية المشتركة (Block Copolymers) في مذيبات انتقائية (مذيبات جيدة لجزء من البوليمر المشترك وغير جيدة للجزء الآخر بمعنى آخر مذيبة لبوليمر وغير مذيبة للآخر إذا كان البوليمر المشترك يتكون من بوليمرين ويتكون كل من هذه البوليمرات المشتركة من لب (جوف) ذو كثافة عالية يتألف في كتلة غير ذائبة وغلاف يتألف من كتلة ذائبة.

من أهم خصائص هذه البوليمرات المكونة للمذيبات هي الوزن الجزيئي للمذيلات وعدد التجمع (عدد جزيئات البوليمر المشترك في المذيلة الواحدة)، حجم اللب وحجم الغلاف وكثافة اللب وكثافة الغلاف كقاعدة تكون جزيئات البوليمرات المشتركة في المذيلات في حالة توازن ديناميكي مع جزيئات البوليمر غير الموجود في المذيلات. إن ديناميكية وحركية هذا التوازن وتفكك المذيلات هي من الخصائص الهامة التي يجب دراستها. إضافة إلى الطرق المذكورة أعلاه توجد طرق هامة أخرى مثل التشتت بواسطة أشعة إكس والتشتت بالنيوترون والتفلور ووقف الانسياب والطرق الحرارية وغيرها.

نظراً لخصائصها المتميزة فإن مذيلات البوليمرات المشتركة تجد لها تطبيقات واسعة في المجالات الزراعية والبيئية وفي صناعة الأدوية والدهانات وغيرها.

جميع هذه التطبيقات سيتم التطرق إليها خلال المحاضرة.

**Keywords :** - Molecular characterization of polymer, Branching, Copolymer micelles.

## ABSTRACT

Basic molecular characteristics of polymers are: molecular architecture, molecular weight and size, and their distributions. All these characteristics are derived from measurements of very dilute solutions. Methods of characterization can be roughly divided into two categories: (i) Direct (also called absolute) methods, in which only measured values and physical constants are needed for the evaluation of a given molecular characteristic (e.g. static and dynamic or osmometry), and (ii) indirect methods, in which either a calibration with polymer samples of known value of the given property must be employed or a polymer structure and shape of the polymer molecules under study must be known (e.g. viscometry, sedimentation, and gel permeation chromatography).

Block copolymers, when dissolved in selective solvents (both organic and aqueous) that are thermodynamically good for one block and poor for the other, and undergo a self-association in which spherical micelles of a nearly uniform size are formed with insoluble blocks in the core and soluble blocks in the shell. A micelle typically consists of ten to a few hundreds of copolymer molecules. Copolymer micelles have been studied for about three decades and are interesting not only from the viewpoint of academic research, but also for their potential applications as motor oil additives, emulsifiers, dispersing and foaming agents, thickeners, solubilizers and, mainly, as vehicles for a targeted drug delivery. Block copolymer micelles just like micelles of soaps and surfactants, are in a dynamic equilibrium with unassociated molecules, called unimers. Various methods are being used for the characterization of the micellar solutions. Combined experimental data of static light scattering, dynamic light scattering and small-angle X-ray (or neutron) scattering provide basic characteristics of micelles: micellar molar mass, micelle hydrodynamic radius, geometric radius of the core and the thickness of the shell. Sedimentation velocity gives us the unimer/micelle mass ratio and, like steady-state fluorescence, also an information about the dynamics of the unimer - micelle equilibrium. Kinetics of micelle formation and micelle dissociation induced by abrupt changes in temperature or in a solvent selectivity, can be determined by stopped-flow instrumentation with static light scattering detection. Very unique information on segmental dynamics in the core and in the shell can be drawn from either NMR or time-resolved fluorescence.

### 1. Introduction

Polymers can be characterized on many levels and from various viewpoints. Roughly, we recognize submolecular, molecular and supermolecular characterization.

(a) supermolecular characterization concerns chemical and configurational properties of small parts of a polymer molecule. We are interested in chemical side groups, tacticity (trans or gauche), or an arrangement of monomer units (e.g. polybutadiene can be formed by 1,2 or 1,4 units, the latter may be cis or trans).

(b) Molecular characterization concerns structure and properties of polymer molecules, studied in their dilute solutions.

(c) Supermolecular characterization deals with ensembles of polymer molecules, either in solutions (molecular complexes, aggregates, associates) or, mainly, in bulk. In the latter case we study relation between polymer morphology and various properties (mechanical, optical, rheological, electrical, etc).

All these characteristics are interconnected with the properties of a given polymer. For example, 1,2 - 1,4 - cis, and 1,4 - trans polybutadienes differ in their properties, like crystallinity and  $T_g$ . Various mechanical, rheological and other properties depend on molar mass or on the presence of branching (cf. low - density and high - density polyethylenes).

The aim of this article is to survey briefly some aspects of molecular characterization of polymer molecules and molecular associates - block copolymer micelles.

## 2. Properties of polymer molecules

Properties of polymer molecules are experimentally studied in their dilute solutions. We recognize static and dynamic properties.

### Static properties:

(i) Architecture. Homopolymers (formed by only one kind of monomer units) can be linear or branched. Copolymers (formed by two or more kinds of monomer units) can be statistical, alternating, block and graft).

(ii) Molecular weight or molar mass (the first is dimensionless, the second is in g/mol, numerically are the same). Only biopolymers may be monodisperse, man-made polymers are always polydisperse. Polydispersity in molecular weight can be described by a distribution curve or, more often by a ratio of molecular weight averages,  $M_w/M_n$ .  $M_n$  equals  $\sum N_i M_i / \sum i M_i$  and  $M_w$  equals  $\sum N_i M_i^2 / \sum N_i M_i$ , where  $N_i$  is a number of molecules of molecular weight  $M_i$ .

(iii) Size of a macromolecule can be measured either as the radius of gyration,  $R_G$ , or the hydrodynamic radius,  $R_H$ .  $R_G$  is defined as a root-mean square of the average distance of a mass element from the centre of mass of a polymer molecule,  $R_H$  as a radius of a hard sphere, which has the same hydrodynamic property, as the particle under study.

### Dynamic properties

Dynamic properties of polymer molecules can be studied in dilute solutions in steady state (diffusion, segmental dynamics) or under application of an external force (sedimentation, viscosity, electrophoretic mobility).

All static and dynamic characteristics (with exception of molecular architecture and molecular weight) are influenced by thermodynamic quality of a solvent in which a given property is measured. Usually, this influence is eliminated

by extrapolation of a measured value to infinite dilution.

## 3. Experimental methods

Numerous physico-chemical methods are employed to characterize static and dynamic properties of polymer molecules. Basically, they are either direct (or absolute) ones, in which a given characteristic (e.g.,  $M$  or  $R$ ) can be obtained from a measured value (e.g., intensity of scattered radiation, osmotic pressure, etc.) and physical constants, independent of the individual property of a given system, or indirect (or relative) ones, in which either a calibration with polymer samples of a known value of a given property must be employed, or a polymer structure and shape of the polymer molecules under study must be known.

Description of the methods used for polymer molecular characterization can be found in all basic textbooks of polymer chemistry<sup>1-3</sup>. Here, only enumeration of a few basic methods is in Table 1.

## 4. Characterization of Block Copolymer Micelles

Block copolymers in solutions in selective solvents, that are good for block and poor for the other, self-associate forming multimolecular micelles, the cores of which consist of insoluble blocks, while the soluble blocks are located in protective shells. A typical association number (i.e. the number of copolymer molecules in a micelle) is from tens to hundreds. These micelles, with a narrow molar mass and size distribution, are in dynamic equilibrium with molecularly dissolved copolymer molecules (unimers). Unlike aqueous micellar systems of soaps and surfactants, block copolymer micellar systems in both organic and aqueous selective solvents have very low, usually imperceptible, critical micelle concentration (CMC). The structure and various properties of these micelles have been studied by numerous physico-chemical methods (Table 1) and the results have been reviewed several times<sup>4-6</sup>. Most of the studies in 60s, 70s and earlier 80s were performed with block copolymers in organic solvents nowadays studies in aqueous systems prevail. Some typical micellar systems are in Table 2.

Block copolymer micelles are interesting not only from the academic viewpoint, they found various applications as,

e.g., motor oil additives, dispersing and foaming agents, thickeners, solubilizers and, mainly, as vehicles for a targeted drug delivery.

From various properties of block copolymer micelles, only those concerning micellar structure, dynamics of micellar equilibria, and kinetics of micelle formation and dissociation will be mentioned, to illustrate an employment of a combination of experimental techniques.

#### (a) Micellar molar mass and size

Micellar molar mass is usually measured by static light scattering (SLS), provided unimer  $\leftrightarrow$  micelle equilibrium is shifted towards micelles. If the unimer is present in a substantial amount, SLS provides - at a finite copolymer concentration - only an apparent molar mass, for the closed association defined as

$$M_w^{\text{app}} = M_w^{(u)}W^{(u)} + M_w^{(m)}W^{(m)} \quad (1)$$

where superscripts (u) and (m) stand for unimer and micelles, respectively, and  $w$  is the weight fraction. Since the  $M_w^{(u)}$  can easily be determined by SLS in a good solvent, and  $w$  values from sedimentation velocity,  $M_w^{(m)}$  can be calculated. A constant value of  $M_w^{(m)}$  at different copolymer concentrations was considered to provide an experimental proof of the closed - association mechanism of micelle formation process.

The essentially uniform character of micelles has been verified by electron microscopy, by dynamic light scattering (single - exponential decay curves), by sedimentation velocity (sharp concentration boundaries), and by the small - angle X- ray and neutron scattering. (SAXS and SANS) (prominent side maxima on scattering curves).

Micellar size can be characterized by the radius of gyration,  $R_G^{(m)}$ , (from SLS, SAXS, or SANS), or by the hydrodynamic radius,  $R_h^{(m)}$ , (from DLS).  $R_G^{(m)}$  values are practically always apparent values, since the core and the shell have generally different scattering contrasts with respect to the solvent used.

$$(R_G^{(m)})^2_{\text{app}} = Y^{(c)}(R_G^{(c)})^2 + Y^{(s)}(R_G^{(s)})^2 \quad (2)$$

Superscripts (m), (c), and (s) stand for micelle, core, and shell, respectively, and  $Y$  is the contrast. Assuming a simple concentric - sphere model eq. (2) can be rewritten in terms of the geometrical radii of the core,  $R^{(c)}$ , and of the whole micelle,  $R^{(m)}$ .

$$(R_G^{(m)})^2_{\text{app}} = 0.6Y^{(c)}(R^{(c)})^2 + 0.6Y^{(s)}(I/J) \quad (3)$$

where  $I = (R^{(m)})^5 - (R^{(c)})^5$  and  $J = (R^{(m)})^3 - (R^{(c)})^3$ . Since  $R^{(c)}$  can be determined from the position of the side maximum on the SAXS or SANS scattering curves,  $R^{(m)}$  and the thickness of the shell,  $D^{(s)}$  can be calculated. Such experiments have been done for various micellar systems.

Once  $M_w^{(u)}$ ,  $M_w^{(m)}$  copolymer composition,  $R^{(s)}$ , and  $D^{(s)}$  are known, the association number, the average segment densities in the core and in the shell, as well as the average dimensions of the core - forming and shell - forming blocks, can be calculated and compared with theoretical predictions.

To give a typical example<sup>7</sup>, a triblock copolymer with polystyrene outer blocks and hydrogenated polybutadiene middle block ( $M_w^{(u)} = 74\,000$ , 30 wt.% styrene) forms micelles with aliphatic cores and polystyrene shells in dioxane. Association number of micelles is 70,  $R^{(c)} = 12.5$  nm,  $D^{(s)} = 10$  nm, average segment densities of the core and the shell are 0.74 and 0.06, respectively.

#### (b) Unimer $\leftrightarrow$ micelle equilibrium

The micellar equilibrium state is given by a minimum of the Gibbs energy of the system. It has been found that polymer micelle formation in organic selective solvents is an enthalpy - driven and entropy - controlled process. Surfactant and some polymer micelle formation in water is, on the other hand, an entropy- driven process, due to the effect of hydrophobic interactions and the consequent change of water structure.

Unimer  $\leftrightarrow$  micelle equilibrium represents a dynamic process, in which copolymer molecules migrate at a given rate between micellar and unimer states, i. e. also, between micelles themselves. Two methods have been employed, probing the dynamics of micellization equilibria: Steady-

state fluorescence and sedimentation velocity<sup>8</sup>.

Steady - state fluorescence: Core- forming block of one portion of a copolymer sample is labeled by fluorescence donor (e.g. carbazol), second by a fluorescence acceptor (e.g. anthracene). Micellar solutions of the two differently labeled samples are mixed and exchange of copolymer molecules between micelles, i. e., formation of carbazol-tagged and anthracene- tagged micelles, can be monitored as the nonradiative energy transfer from carbazol to anthracene groups. Equilibration process proved to be much slower than in case of soap and surfactant micelles, it is usually on a time scale of hundreds or thousands seconds.

Sedimentation velocity: Two kind of micelles with different molar masses and sizes (and thus with different sedimentation coefficients) are mixed, and the formation of mixed micelles with an intermediate sedimentation coefficient is monitored with an analytical centrifuge. Two different original concentration boundaries, approaching each other in time, indicate that the equilibration proceeds via exchange of copolymer molecules between smaller and larger micelles. While in case of block copolymer micelles in organic solvents this process is on time scale  $10^2 - 10^3$  s, in case of aqueous media is much slower and in some cases, when cores of micelles are glassy, equilibrium is frozen.

### (c) Kinetics of micelle formation and dissociation

While numerous studies have been devoted to the kinetics of micellization of soaps and surfactants in water, kinetics data on block copolymer micelle formation are scarce. In one of few works<sup>9</sup>, the stopped flow method with light scattering detection was employed to study rates of micelle formation and dissociation with a diblock AB and a triblock ABA copolymers, A being styrene, and B hydrogenated polydiene. Micelle formation was realized by mixing a molecular solution in a good solvent with a precipitant, so that the final solvent mixture became selectively bad for block B. Micelle dissociation was realized by mixing a micellar solution with a good solvent, so that the final solvent mixture became thermodynamically good for both blocks. The results can be summarized as follows. The relaxation time for micelle formation was on the same time scale (tens of ms) for both samples. Relaxation time of micelle dissociation for the diblock copolymer was shorter than one ms, while the triblock copolymer was over 100 ms. The interpretation of these

results, taking into account the shapes of the intensity- time dependences, was: Micelle formation proceeds in two steps: In the first one, B blocks shrink and copolymer molecules get together. In the second stage, the B block in the core rearrange, finding their low- entropy conformations. In case of triblock copolymers, these block may get entangled. In the dissociation process, the first step is a rapid influx of solvent molecules into the micellar core, the second step is a separation of copolymer molecules. Dissociation of the triblock copolymer micelles is slowed down by a disentanglement process. A strongly non - single exponential character of the intensity - time dependence in the latter case indicated that the process is accompanied and complicated by a slow exchange of unimers between micelles.

**Table 1. Some experimental methods for molecular characterization of polymers**

A given characterization	Direct methods	Indirect methods
Molecular weight	Osmometry ( $M_n$ ) Static light scattering ( $M_w$ ) Small-angle X-ray scattering ( $M_w$ ) Small- angle neutron scattering ( $M_w$ )	Viscometry ( $M_v$ ) Gel permeation chromatography ( $M_{GPC}$ ) Sedimentation velocity ( $M_s$ )
Distribution of M	Fractionation Gel permeation chromatography with light scattering detection	Sedimentation equilibrium Gel permeation chromatography
Molecular size	Static light scattering ( $R_G$ ) Small-angle X- ray scattering ( $M_G$ ) Small- angle neutron scattering ( $M_G$ ) Dynamic light scattering ( $R_H$ )	Viscometry ( $R_H$ )

**Table 2. Some experimental methods for characterization of polymers MICELLES**

Method	Abbr	Information obtained
Static light scattering	SLS	Weight - average molar mass Radius of gyration
Small - angle X- ray and neutron scattering	SAXS SANS	Weight - average molar mass Radius of gyration Core radius
Dynamic light scattering	DLS	Diffusion coefficient Hydrodynamic radius
Electron microscopy	EM	Size and shape
Sedimentation velocity	SV	Unimer/micelle mass ratio Dynamics of micellar equilibria
Size exclusion chromatography	SEC	Dynamics of micellar equilibria
Stopped - flow	SF	Kinetics of micellar formation and dissociation
Steady - state and Time - resolved fluorescence	SSF TRF	Dynamics of micellar equilibria Dynamics on segmental level
Nuclear magnetic resonance	NMR	Dynamics on segmental level

**TABLE 3. SOME TYPICAL MICELLAR SYSTEMS**

Copolymer	Solvent (selectively good for)
PS- b- PMMA	P- xylene (PS)
PS- b- P1	acetone (PMMA)
PS - b- PB - b - PS	dimethylformamide (PS)
PS - b - PDMS	hexane (P1)
PS - b - PAAc	methyl ethyl ketone (PS)
PEO- b -PPO -b- PEO	decane (PDMS)
PS -b - PEO	water (PAAc)
	water (PEO)
	water (PEO)

PS.. polystyrene, PMMA.. poly (methyl methacrylate), P1.. polyisoprene, PB.. polybutadiene, PDMS.. poly (dimethylsiloxane), PEO.. poly (ethylene oxide), PPO.. poly (propylene oxide)

**References**

1. **P. J. Flory:** Principles of Polymer Chemistry, Cornell University Press, Ithaca, N. Y. 1953.
2. **H. Morawetz:** Macromolecules in Solution, Wiley, N. Y. 1965.
3. **P. Munk :** Introduction to Macromolecular Science, Wiley, N. Y. 1989.
4. **G. Riess, G. Hurtrez, and P. Bahader,** in: Encyclopedia of Polymer Science and Engineering, Vol. 2, H. F. Mark, ed., N. Y. 1985.
5. **C Price, in:** Development in Block Copolymers, Vol. 1, I Goodman, ed., Appl. Sci. Publ. London and N. Y. 1982.
6. **Z. Tuzar and P. Kratochvil,** Surf. Colloid Sci. 15, 1 (1993).
7. **Z. Tuzer , J. Plestil, C. Konak, D. Hlavata, and A. Sikora,** (1983) Makromol. Chem. 184, 2111 (1983).
8. **Z. Tuzer, (1992) J. Macromol. Sci., Macromol. Reports, A29, 173 (1992).**
9. **B Bednar, K. Edwards, M. Almgren, S. Tormod, and Z. Tuzer, (1998) Makromol. Chem., Rapid Commun 9, 785 .**