

**PLEISTOMERS. THEORETICAL PREDICTIONS
AND EXPERIMENTAL FINDINGS**

MARIA BERCEA

*“Petru Poni” Institute of Macromolecular Chemistry, 41-A,
Grigore Ghica Voda Alley, 700487 Iasi, Romania
bercea@icmpp.ro*

*This paper is dedicated to the memory of
Acad. Cristofor I. Simionescu (1920–2007)
on the commemorative celebration of his birth centenary.*



Acad. Cr. I. Simionescu at the Technology
of Macromolecular Compounds Course, 1985 class

The paper reviews the scientific achievements reported by the school of polymers founded by Acad. Cristofor I. Simionescu in the field of pleistomers (ultrahigh molecular weight polymers). During the 80's and 90's, many efforts were devoted to their synthesis and characterization, and here Simionescu and coworkers have made a substantial contribution. Plasma-induced polymerization was successfully used for the first time to obtain very long macromolecular chains with unusual properties. By using different techniques, systematic studies were carried out in dilute solution and solid state, for

determining the conformational characteristics of pleistomers. New thermodynamic approaches were tested and validated experimentally for the very high molecular weight range of polymers. Semidilute solutions of pleistomers were used as model fluids for testing the new rheological concepts for polymers in entangled state.

Keywords: pleistomers, plasma-induced polymerization, conformational characteristics, excluded volume effect, entangled macromolecules

1. INTRODUCTION

From the first evidence of its existence, a *polymer* denotes a chemical species composed by many repeating parts (from the Greek, *πόλες* = many; *μέρος* = part), *i.e.*, a long macromolecule containing a certain number of repeating units, N , coming from monomers, that gives the degree of polymerization. The molecular weights of such compounds cover a large range, usually from a few thousands to hundreds of thousands units (g/mol).

The size of the macromolecular chains is one of the most important characteristics of polymers [1–3]. If the dimensions of macromolecules are known, along with their structure and conformation, many properties of interest, such as the rheological or mechanical ones, can be predicted and exploited in practical applications.

For the first time, the ultrahigh molecular weight (u.h.m.w.) polymers were called by Simionescu *et al.* [1] **pleistomers** (*pleistos* = very many, so pleistomers mean *very many mers*). The term pleistomers was attributed to very long macromolecular chains, with molecular weights of millions of units (g/mol), representing more than 15–20 thousands of repeating structural units [1–3].

The lower limit of the molecular weight domain corresponding to polymers is characteristic to each type of structure, being mainly influenced by chain flexibility. Inferior homologues are known as *oligomers*, also denoted as *pleinomers* [4], characterized by a number of repeating structural units (N) in the $2 < N < N_o$ range, where N_o is the critical number of structural units above which the characteristic polymer properties are observed.

For a clearer image of the variation of chain dimensions, Figure 1 schematically delimitates the different domains of polymers as a function of their physical properties – for example, under good solvent conditions, the mean radius of gyration for pleistomers can reach hundreds of nanometers up to micrometers [1–3,22,23,40,59,68]. For oligomers, the dimensions are below 10 nm while, for usual length polymers, the macromolecular size reaches tens and hundreds of nanometers (50–250 nm) [68].

From the dependence of intrinsic viscosity and molecular weight (or N) it was observed that, generally, $N_o > 20$. For example, N_o was 28 for rigid macromolecules of xanthan [5,6], 50 for polystyrene [7,8], 75 for polyacrylonitrile [2,3] and 135 for very flexible chains, poly(dimethylsiloxane), respectively [9].

Due to the polydispersity of samples, the transition from oligomers to polymers covers sometimes a range of molecular weights, a limit that can be depicted by following the thermodynamic or thermomechanical properties as a function of molecular weights.

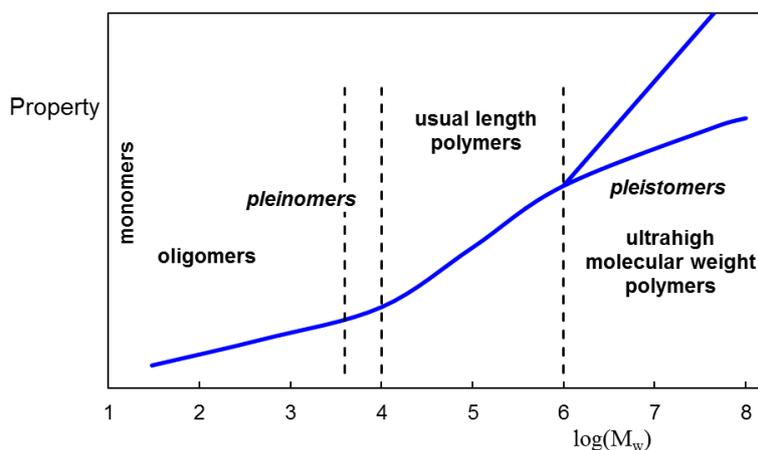


Fig. 1. Delimitation of different molecular weight domains as a function of the change in the properties of a homologous series. “*Pleistomers*” denote very long macromolecular chains, a concept firstly introduced by Simionescu *et al.* [1].

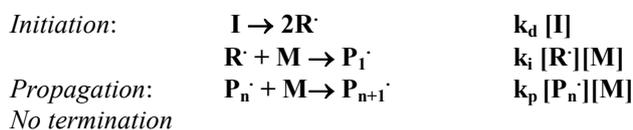
As the macromolecular features were more and more extensively elucidated, a new question appears: how do polymers behave when the molecular mass increases highly, of the order of millions of units (g/mol). Considering that chain flexibility increases with increasing molecular weight, and extrapolating this observation to very high molecular weights, one can reach an artifact and postulate erroneous conclusions, with no physical meaning. Thus, any theoretical hypothesis must be supported and validated by experimental data.

The two extreme molecular weight species, *pleinomers* and *pleistomers*, represent not only quantitative forms of homologous series, but also they have distinct features, compared with usual length polymers.

2. PLASMA-INDUCED POLYMERIZATION – A NEW ROUTE FOR PLEISTOMERS SYNTHESIS

The synthesis of u.h.m.w. polymers was reported by using an original procedure reported by Simionescu *et al.* in a series of papers issued in the 80’s [10–26]. These studies confirmed the experimental evidence on living radical polymerization by using plasma-induced (co)polymerization as a technique for obtaining living macroradicals. In addition, a kinetic model of untermi-

polymerization was proposed [24]. Usually, the free radical polymerization kinetics assumes three different stages: initiation, propagation and termination. In the first stage, initiator's decomposition takes place, in order to produce two free radicals (\mathbf{R}^{\cdot}). By adding monomer (\mathbf{M}) molecules, initiation of the active polymer chain (\mathbf{P}^{\cdot}) occurs. In the second step, the active chain propagates and the macromolecule grows by adding new monomer molecules. This process stops either by chain transfer reactions to \mathbf{X} (\mathbf{X} = monomer, initiator, solvent, impurity, chain transfer agent, etc.), or by a recombination/ disproportionation reaction with another active chain. For plasma-induced (co)polymerization process, the initiation reaction occurs in the gaseous phase. The active species are formed very fast and the activity of the propagating chains is very high and stable in time, even at room temperature, yielding very high or ultrahigh molecular weight polymers. The last stage is missing and the polymerization in such conditions presents a living character (Scheme 1), as demonstrated by the following characteristics: the transfer and termination steps were eliminated or drastically diminished; concentration of the used initiator was very low; polymerization was carried out in the absence of impurities; due to the high viscosity of the environment, the mobility of growing macroradicals was considerably reduced, inducing a living character to the polymerization process. Also, a prolonged post-polymerization period was required as, within about 400 hours, relative viscosity increased 200 times while M_w reached values of 10^7 g/mol, with a low conversion (below 3%) [24]. For the kinetic expressions written on the right side of Scheme 1, it was assumed that radical reactivity is independent on chain length; the radicals resulted in chain transfer reactions reinitiate the propagation of chains; the monomer is consumed completely during propagation.



Scheme 1. Kinetic model of plasma-induced polymerization (adapted from [24])

3. CONFORMATIONAL CHARACTERISTICS IN SOLUTION

The thermodynamic properties of pleistomers in solution were discussed from the viewpoint of their dependence on solvent quality and molecular weight, at different temperatures of interest. The results were published in more than 100 papers reported by Simionescu's group, some representative contributions being included in the reference list [1–3,7,8,22,23,25,27–35,37–74].

The specific interactions occurring in u.h.m.w. polymer solutions were carefully studied from both theoretical and experimental points of view. It was demonstrated that the increase of macromolecular size is accompanied by the

appearance of new properties, which requires reconsideration of the fundamental laws governing the physico-chemistry of polymers [1–3].

The thermodynamic behaviour of dilute polymer solutions, quantified through the conformational characteristics, influenced by temperature, solvent quality, molecular weight domain, can be approached by different excluded volume theories. Such theoretical approaches mutually differ in the mathematical methods and approximations used, yet all of them relate the excluded volume effects to measurable quantities, by considering different possible interactions (polymer-solvent, short- and long-range, intra- and intermolecular interactions).

Solvent quality plays an important role in determining the type and magnitude of polymer-solvent interactions. Thus, in a *good solvent*, the attraction forces between the chain segments are weaker than the polymer-solvent interactions, so that the random coil adopts an extended conformation. The excluded volume interaction is responsible for the swelling behaviour of the overall chain dimensions in a good solvent, and the polymer is dissolved over a wide range of temperatures.

In a *poor solvent*, the polymer-solvent interactions are not favored, and therefore the attraction forces between chains predominate, consequently the random coil adopts a contracted conformation. The situation when the second virial coefficient is zero, known as θ (*theta*) *state*, depends on the polymer-solvent system and temperature. In this state, the polymer chains behave as ideal ones, the interactions of monomer units distanced from each other along the chain being neglected. Any polymer can reach its θ state, either choosing the appropriate solvent (named θ *solvent*) at constant temperature, or adjusting the temperature (named θ *temperature* or *Flory temperature*) in a given solvent. The unperturbed dimensions of pleistomers are influenced by the occurrence of unhindered interpenetration, which diminishes the preferential adsorption phenomena [8]. Thus, no conformational transition phenomena depicted for usual length polymers in the vicinity of theta condition were observed at high molecular weight polymers [2,39,46,50,58,67].

The following conformational characteristics of macromolecules were investigated: the second virial coefficient (A_2), the mean dimensions (R_g or $\langle S^2 \rangle^{1/2}$), intrinsic viscosity [η]. They express the thermodynamic behaviour of macromolecules in dilute solutions and are influenced by temperature and solvent quality, on one hand, and by polymer's structure and architecture, by electrostatic interactions and polymer concentration, on the other. Many efforts were devoted in Simionescu's group to explore the influence of the molecular weight domain upon the conformational characteristics of oligomers and polymers.

In the oligomer region, the effect of the excluded volume is negligible, even in good solvent conditions [73,74], when the unperturbed state is attained and the chains present a Gaussian behaviour. The excluded volume effects become important in good solvents, as the dimensions of polymer chains increase. There are different concepts trying to describe the thermodynamic behaviour of macromolecules by using dimensionless parameters, such as the excluded volume

parameter (z), the second virial coefficient (A_2) or the Flory-Huggins interaction parameter (χ). The theoretical approaches mutually differ in the mathematical methods and approximations adopted, but all of them relate the dimensionless parameters to measurable quantities, by considering different possible interactions. These interactions will influence the conformation and configuration of polymer chains and, consequently, their thermodynamic behaviour. A single macromolecular chain can be fully extended in good solvents at high dilution (high excluded volume effect), but usually a macromolecular coil is formed, due to the balance of interactions with the solvent and polymer itself. In addition, understanding the dynamics of polymer chains is the key for predicting the properties of polymer solutions, such as diffusion coefficients, viscosity, sedimentation coefficient, and rheological characteristics.

The conformational characteristics of different pleistomers were investigated by the research group of Simionescu in good and theta solvents. Some conclusions were directly drawn from the experimental data concerning the root-mean square radius of gyration, S , the second virial coefficient, A_2 , and intrinsic viscosity, $[\eta]$. Different models and extrapolation procedures were also tested for pleistomers, the application of which requires a careful analysis of results. It is now generally accepted that the most important parameters characterizing the conformational characteristics of polymers in dilute solutions, denoted as P , depend on the molecular weight of polymers, M , according to the following relationship [2,3]:

$$P = K_p \times M^a \quad (1)$$

where K_p is a proportionality constant depending on the thermodynamic conditions (solvent quality and temperature).

The following limits were established for the conformational characteristics of pleistomers:

$$\begin{array}{lll} P = S & \Rightarrow & a_S = 0.5 \quad \text{theta conditions; } a_S \rightarrow 0.6 \text{ good solvent} \\ P = A_2 & \Rightarrow & A_2 = 0 \quad \text{theta conditions; } a_{A_2} \rightarrow -0.2 \text{ good solvent} \\ P = [\eta] & \Rightarrow & a_\eta = 0.5 \quad \text{theta conditions; } a_\eta \rightarrow 0.8 \div 0.9 \text{ good solvent} \end{array}$$

With increasing molecular weight, in the same thermodynamic conditions, there is a change in the values of K_p and a ; thus, for high excluded volumes (pleistomers in good solvents), exponent a tends to asymptotic values [2,3,73].

4. EXCLUDED VOLUME EFFECT

The interactions involving the isolated macromolecules manifested in dilute solutions are conveniently divided into two classes:

– Short-range interactions, which occur between neighboring atoms or groups, and are usually forces of steric repulsion caused by the overlapping of electron clouds;

– Long-range interactions, consisting of attractive or repulsive forces between segments widely separated in a chain that occasionally approaches one another during molecular flexing, and between polymer segments and solvent molecules.

Different approaches are included in the two-parameter theory that postulates that the second virial coefficient, A_2 , intrinsic viscosity, $[\eta]$, and the static (α_s) and viscometric (α_η) expansion factors are functions of short-range and long-range interactions through the interpenetration function, $\Psi(z)$ [75–77]. Very briefly, the behaviour of flexible polymers in dilute solution is usually done through some dimensionless parameters, namely [2,3]:

– excluded volume parameter, z , defined as:

$$z = [1/(4\pi)]^{3/2} (B_L / A^{3/2}) M^{1/2} \quad (2)$$

where: $B_L = \beta / m^2$ (B_L is the long range interaction parameter; β is the binary cluster integral between macromolecule's repeating units of molecular weight m); $A = S_\theta^2 / M$, S_θ – the mean radius of gyration in unperturbed state, M – molecular weight of polymer;

– linear expansion factors, α_s and α_η :

$$\alpha_s = S^2 / S_\theta^2 \quad (3)$$

$$\alpha_\eta^3 = [\eta] / [\eta]_\theta \quad (4)$$

where: S^2 , S_θ^2 and $[\eta]$, $[\eta]_\theta$ represent the mean square radii of gyration and intrinsic viscosity in perturbed and unperturbed state, respectively;

– the interpenetration function, $\Psi(z)$:

$$\Psi(z) = A_2 M^2 / (4\pi^2 N_A S^3) \quad (5)$$

where N_A – Avogadro's number;

– the hydrodynamic penetration function, $\pi(z)$, which can be expressed as:

$$\pi(z) = A_2 M / [\eta] \quad (6)$$

Figure 2 shows the general shape of $\pi(z)$ (which is very similar to $\Psi(z)$), evidencing that, for high excluded volume (extended conformation of pleistomers), $\pi(z) \rightarrow 1.1$ [2,3].

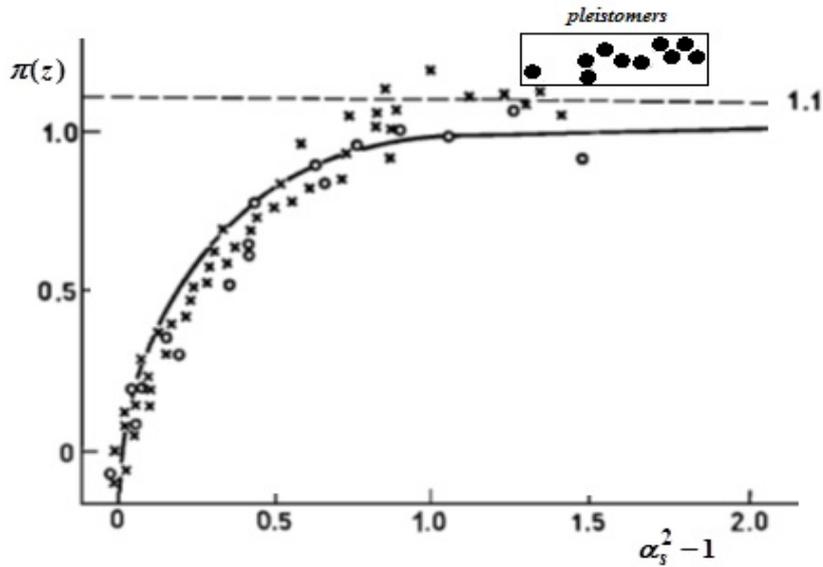


Fig. 2. Hydrodynamic penetration function, $\pi(z)$, as a function of linear expansion factor, $\alpha_s^2 - 1$, for pleistomers in solution [3], compared with usual length polymers (data summarized in [75]). The full curve is given by the theoretical predictions [76,77] (adapted from [3] with permission from Elsevier).

A major deficiency of the excluded volume theories lies in the fact that the most approximate equations frequently emerge from first-order perturbation calculations, and the required mathematical transformations are only permitted for infinite molecular weight. Thus, experimental data is still needed for pleistomers on order to formulate the general expression for the behaviour of macromolecular chains in solution.

5. SEMIDILUTE SOLUTIONS OF PLEISTOMERS AS MODEL FLUIDS

Most single long polymer chains present high elasticity and are very extendable under stress. For the mathematical description of the large-scale deformations exhibited by a Gaussian polymer chain (considered as beads connected by a spring and surrounded by fluid molecules), two models were widely used: Rouse model, where excluded volume and hydrodynamic interactions are neglected, and Zimm model, which takes into account the hydrodynamic interactions [78,79]. During the shear flow, the isolated macromolecules in dilute solution suffer alternative stretching and contraction. By stopping the external force which determines the flow, the polymer chains tend to find their equilibrium

end-to-end distance controlled by entropy through an elastic force. Nevertheless, flexible and semi-flexible chains in dilute solution do not show any elastic recovery, due to a lack of chains connexion, despite the fact that the chains extend/ recoil by applying/ stopping the external stress. Thus, elastic recovery is usually detected in concentrated polymer systems where temporary junctions are present, connecting/ associating all chains to the boundaries of the sample.

However, by increasing molecular weight, the viscosity of polymers in solution or melt state also increases, due to the higher resistance manifested when external forces are applied, so that processing of such materials becomes very difficult. In semidilute solution, pleistomers have different properties, as compared with usual lengths polymers.

The macromolecular features of pleistomers in semidilute solutions can be described on the basis of the *reptation* concept, which was the starting point for a revolutionary approach describing the macromolecular dynamics in solution or in melt state. According to this theory [80], each polymer chain is confined within a virtual *tube* made up of the neighboring chains. The Doi-Edwards theory [80] and its variations [81–85] give nowadays a satisfactory prediction for the time-dependent flows in complex fluids [72]. The Doi-Edwards approach gives a reasonable description of the macromolecular response to large step-shear strains, but fails to predict other nonlinear shear properties, such as the steady-state viscosity or the relaxation of stress after cessation of steady shearing [64].

To describe the rheological behaviour of entangled polymers at very high shear rates, Cates *et al.* [86] have proposed a new mechanism for chain stretching, which arises because the tube, even when fully aligned with the flow, has a finite lateral dimension, which exposes different parts of the chain to different flow velocities. Using a simplified model, the authors predict the asymptotic behaviour of the shear stress and a first normal stress difference, and show that stable flow is recovered at sufficiently high shear rates. This new approach also predicts a quasi-plateau of shear stress (rather than a true one), which becomes flatter and flatter as the number of entanglements per chain increases. Experimentally, a true plateau of stress evolution as a function of shear rate cannot be observed in melts or concentrated solutions of synthetic polymers with ordinary molecular weights. At the same time, it should be noted that experiments performed at high shear rates often show serious difficulties (for instance, in cone-and-plate experiments, the sample can be expelled from the apparatus). These difficulties were overcome by using semidilute solutions of extremely long chains. Thus, the first validation of this model was signaled previously for u.h.m.w. poly(methyl methacrylate) [48,50] and a more detailed experimental study was presented later [72]. High molecular weight polymers (usually, with M_w above 10^6 g/mol) have a very large spatial extension and interpolymer interactions occur at low concentration. As for moderate-to-high molecular weight polymers, a large difference in the rheological behaviour occurs over a critical concentration, c_e , where chain entanglements begin to take place. The viscosity scales with M below c_e while it scales as $M^{3.5}$ above c_e [50].

The response of a viscoelastic fluid to a step strain deformation is governed by two characteristic times, the equilibration or retraction time (τ_e) and the reptation or disengagement time (τ_d), which characterizes the escape of the chain from its constrained environment. At times just after the strain step, an extended chain retracts rapidly inside the affine deformed tube, which constrains it, and the stress relaxes rapidly with a characteristic time τ_e [78]. The value of the retraction time, τ_e , is on lower than the longest relaxation time τ_R of a Rouse chain. At times enough longer than τ_e , the chain disengages itself from the tube and gradually assumes a random orientation by *reptation*, which takes place in a time τ_d , called the disengagement time, which is approximately equal to the longest relaxation time of the fluid. An empirically determined material time constant τ_k is often defined for a fluid by the time after which the stress relaxation modulus can be factored into time and strain dependent functions, the so-called time and strain-dependent factorability [85]. Values of τ_k represent the end of the retraction process, or times sufficiently higher than τ_e . The alignment approximation in the Doi-Edwards theory gives a satisfactory prediction for the general deformation history. Without this prediction, the time-dependent flows have been somewhat limited.

U.h.m.w. poly(methyl methacrylate) in good (toluene) and marginal (dimethylformamide) solvents has shown unusual shear behaviour [72]. It presented a plateau in the viscosity and first normal stress difference curves when plotted against shear rate. At sufficiently low shear rates ($\dot{\gamma} \cdot \tau_d < 1$), the entanglement network is nearly undisturbed. At a flow faster than τ_d^{-1} , the flow stretches the tube; initially, the chain follows it, but then it shrinks back by a retraction process. At such high shear rates, Doi and Edward predict that the steady-state viscosity $\eta(\dot{\gamma})$ is a decreasing function of $\dot{\gamma}$: $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-3/2}$. Since $\sigma(\dot{\gamma}) = \eta(\dot{\gamma}) \times \dot{\gamma}$, the shear stress should increase at low shear rate, attaining its maximum at $\dot{\gamma}_1 = \tau_d^{-1}$, and then decreasing at higher shear rate [48,72]. A successful theory was obtained [81–86] by developing a molecular model based on the convective constraint release (**CCR**). The revised model predicts many of the features of steady and transient shearing flows. Convective constraint release can both shorten the reptation tube and allow reorientation of interior tube segments. The general Doi-Edwards theory is re-written in a simplified form, which assumes that all parts of the molecule share the same orientation and degree of stretch or in a contour-variable form in which orientation and stretch are functions of tube coordinates. The resulting theory captures many nonlinear rheological properties of entangled flexible polymers under fast flows, *i.e.*, at shear rates $\dot{\gamma} > 1/\tau_d$ [48,64,66,71,72,82,83]. Thus, semidilute solutions of pleistomers represent ideal systems for testing the new concepts on flow dynamics of polymers in entangled state.

6. OUTLOOKS / PERSPECTIVES?

Pleistomers have penetrated different application areas, including many advanced technologies. As a result, many groups have become more and more concerned with their synthesis [87–95]. In addition, many natural polymers have very long chains [96].

A comprehensive understanding of pleistomers (from their synthesis and characterization to potential applications) still represents a challenge. Application of the fundamental laws governing polymer chemistry and physics to the very large dimensions of the macromolecular chains revealed that many accepted concepts and relations have to be revised or reformulated [2,3]. Thus, a reasonable understanding of pleistomer properties generates new research directions and unexpected end uses, for example: engineering [87,88,91] and biomedical [92] applications, wastewater treatment [90,94], enhanced oil recovery [49,63,95], etc.

REFERENCES

1. SIMIONESCU C.I., SIMIONESCU B.C., IOAN S., *Plasma-induced living radical copolymerization*, J. Macromol. Sci, Part A: Chem: Pure Appl. Chem., 1985, **A22**, (5–7), 765–768.
2. SIMIONESCU C.I., IOAN S., BERCEA M., SIMIONESCU B.C., *Thermodynamic aspects of ultrahigh molecular weight polymer solutions*, Mem. Sci. Sect. Rom. Acad., 1991, **XIV**, 29–79.
3. BERCEA M., IOAN C., IOAN S., SIMIONESCU B.C., SIMIONESCU C.I., *Ultrahigh molecular weight polymers in dilute solutions*, Prog. Polym. Sci., 1999, **24**, (3), 379–424.
4. UGLEA C.V., NEGULESCU I.I., *Synthesis and Characterization of Oligomers*, CRC Press, 1991.
5. CHRISTENSEN B.E., SMIDSRØD O., ELGSAETER A., STOKKE B.T., *Depolymerization of double-stranded xanthan by acid hydrolysis: Characterization of partially degraded double strands and single-stranded oligomers released from the ordered structures*, Macromolecules, 1993, **26**, 6111–6120.
6. BRUNCHI C.E., MORARIU S., BERCEA M., *Intrinsic viscosity and conformational parameters of xanthan in aqueous solutions: Salt addition effect*, Coll. Surf. B: Biointerfaces, 2014, **122**, 512–519.
7. IOAN S., BERCEA M., SIMIONESCU B.C., SIMIONESCU C.I., *Chain conformation and viscometric behaviour of high molecular weight polystyrene in solvent/ nonsolvent mixtures*, Polym. Bull., 1991, **26**, 117–122.
8. SIMIONESCU C.I., IOAN S., BERCEA M., MITU N., SIMIONESCU B.C., *High molecular weight polystyrene in solvent mixtures. Preferential and total adsorption*, Eur. Polym. J., 1993, **29**, (2/3), 183–191.
9. BERCEA M., MORARIU S., BRUNCHI C.E., CAZACU M., Chap. *Solution Behavior of Polysiloxanes*, in *Recent Developments in Silicone-based Materials*, CAZACU M. (Ed.), Nova Sci. Pub., 2010.
10. SIMIONESCU B.C., NATANSOHN A., SIMIONESCU C.I., *Plasma-induced polymerization .1. Bulk copolymerization of methyl-methacrylate and styrene*, Polym. Bull., 1980, **2**, (12), 809–815.
11. SIMIONESCU B.C., NATANSOHN A., LEANCA M., ANANIESCU C., SIMIONESCU C.I., *Plasma-induced polymerization. 2. Bulk copolymerization of alpha-methyl styrene with methyl-methacrylate and acrylonitrile*, Polym. Bull., 1980, **3**, (4), 247–251.
12. SIMIONESCU B.C., LEANCA M., ANANIESCU C., SIMIONESCU C.I., *Plasma-induced polymerization. 3. Bulk and solution homopolymerization of some vinylic monomers*, Polym. Bull., 1980, **3**, 437–440.

13. SIMIONESCU B.C., LEANCA M., IOAN S., SIMIONESCU C.I., *Plasma-induced polymerization. 4. Low conversion bulk-polymerization of styrene*, Polym. Bull., 1981, **4**, (7), 415–419.
14. IOAN S., SIMIONESCU B.C., SIMIONESCU C.I., *Conformational-changes of methacrylonitrile-styrene copolymers in dilute solutions*, Polym. Bull., 1981, **5**, (9–10), 563–568.
15. SIMIONESCU B.C., NATANSOHN A., LEANCA M., ANANIESCU C., SIMIONESCU C.I., *Plasma-induced polymerization. 5. Bulk copolymerization of methacrylonitrile with styrene*, Polym. Bull., 1981, **4**, (10), 569–576.
16. SIMIONESCU C.I., SIMIONESCU B.C., LEANCA M., ANANIESCU C., *Plasma-induced polymerization. 6. Living macroradicals as macromolecular initiators*, Polym. Bull., 1981, **5**, (2), 61–66.
17. SIMIONESCU C.I., SIMIONESCU B.C., *Plasma-induced polymerization. 7. Some characteristics of this method of polymer synthesis*, Rev. Roum. Chim., 1982, **27**, (1), 141–146.
18. SIMIONESCU B.C., IOAN S., SIMIONESCU C.I., *Plasma-induced polymerization. 8. On the heterogeneity of chain composition of methacrylonitrile-styrene copolymers*, Polym. Bull., 1981, **6**, (1–2), 87–91.
19. SIMIONESCU B.C., IOAN S., POPA M., SIMIONESCU C.I., *Plasma-induced polymerization. 9. Living radical copolymerization of methyl-methacrylate and styrene*, Polym. Bull., 1982, **6**, (8–9), 415–419.
20. IOAN S., SIMIONESCU B.C., SIMIONESCU C.I., *Plasma-induced polymerization. 10. On the heterogeneity and excluded-volume effect of methyl methacrylate-styrene copolymers*, Polym. Bull., 1982, **6**, (8–9), 421–428.
21. SIMIONESCU C.I., SIMIONESCU B.C., *Plasma-induced polymerization. 11. Plasma-induced polymerizations and copolymerizations*, Chemicke Zvesti, 1983, **37**, (5), 685–692.
22. SIMIONESCU C.I., SIMIONESCU B.C., IOAN S., *Solution properties of ultrahigh molecular-weight polymers. 2. Poly(methyl methacrylate)*, Makromol. Chem., Rapid Commun., 1983, **4**, (8), 549–553.
23. SIMIONESCU C.I., SIMIONESCU B.C., IOAN S., *Solution properties of ultrahigh molecular-weight polymers. 1. Methyl methacrylate-styrene 50–50 random copolymers*, Makromol. Chem. – Macromol. Chem. Phys., 1983, **184**, (4), 829–835.
24. SIMIONESCU C.I., SIMIONESCU B.C., *Unconventional radical polymerizations*, Pure Appl. Chem., 1984, **56**, (3), 427–438.
25. SIMIONESCU C.I., SIMIONESCU B.C., IOAN S., *Solution properties of ultrahigh molecular-weight polymers. 5. Conformational-changes of butyl methacrylate styrene copolymers in dilute solution*, Macromolecules, 1985, **18**, 1995–1999.
26. SIMIONESCU C.I., SIMIONESCU B.C., *Plasma-induced polymerization. 12. Low conversion bulk homopolymerization of methyl-methacrylate*, Rev. Roum. Chim., 1985, **30**, (6), 441–445.
27. SIMIONESCU C.I., SIMIONESCU B.C., IOAN S., *Solution properties of ultrahigh-molecular-weight polymers. 6. Poly(butyl methacrylate)*, J. Polym. Sci., Part C – Polym. Lett., 1985, **23**, (3), 121–127.
28. IOAN S., SIMIONESCU B.C., NEAMTU I., SIMIONESCU C.I., *Solution properties of ultrahigh molecular-weight polymers. 10. Viscosity of dilute to moderately concentrated poly(butyl methacrylate) solutions*, Polym. Comm., 1986, **27**, (4), 113–116.
29. IOAN S., LEONTE A., SAVA C., SIMIONESCU B.C., SIMIONESCU C.I., *Solution properties of ultrahigh molecular-weight polymers. 12. Systematic-error sources affecting the discussion of the excluded volume effect*, Acta Polym., 1986, **37**, (9), 533–536.
30. SIMIONESCU C.I., IOAN S., SIMIONESCU B.C., *Solution properties of ultrahigh molecular-weight polymers (pleistomers). 14. Solvent effect on the unperturbed dimensions of poly(butyl methacrylate) chains*, Rev. Roum. Chim., 1986, **31**, (11–12), 995–999.
31. SIMIONESCU B.C., IOAN S., FLONDOR A., SIMIONESCU C.I., *Solution properties of ultrahigh molecular-weight polymers. 15. A viscometric study of poly(isobutyl methacrylate) in different solvents*, Angew. Makromol. Chem., 1987, **152**, 121–131.
32. SIMIONESCU C.I., IOAN S., SIMIONESCU B.C., *Solution properties of ultrahigh molecular-weight polymers. 13. Viscosity molecular-weight relationships and unperturbed dimensions of poly(butyl methacrylate) in various solvents*, Eur. Polym. J., 1987, **23**, (1), 69–72.

33. SIMIONESCU B.C., IOAN S., SIMIONESCU C.I., *Solution properties of ultrahigh molecular-weight polymers. 7. Conformational characteristics of poly(butyl methacrylate)*, J. Polym. Sci., Part B – Polym. Phys., 1987, **25**, (4), 829–838.
34. SIMIONESCU B.C., IOAN S., CHIRIAC A., SIMIONESCU C.I., *Conformational transitions in poly(butyl methacrylate)*, Polym. Bull., 1987, **17**, (5), 439–443.
35. SIMIONESCU C.I., SIMIONESCU B.C., IOAN S., NEAMTU I., *Solution properties of ultrahigh molecular-weight polymers. 1. A viscometric study on the excluded volume effect of poly(butyl methacrylate)*, Polymer, 1987, **28**, (1), 165–169.
36. SIMIONESCU C.I., IOANID A., SIMIONESCU B.C., *Molecular-weight investigation of ultrahigh molecular-weight poly(butyl methacrylate) by electron-microscopy*, Acta Polym., 1987, **38**, (10), 586–588.
37. SIMIONESCU C.I., IOAN S., SIMIONESCU B.C., *Experimental and theoretical data on excluded volume effect of ultrahigh-molecular-weight polymethacrylates*, Makromol. Chem. – Macromol. Symp., 1988, **20/21**, 235–243.
38. SIMIONESCU C.I., IOAN S., FLONDOR A., SIMIONESCU B.C., *Solution properties of ultrahigh-molecular-weight polymers. 16. Unperturbed dimensions of poly(isobutyl methacrylate)*, Makromol. Chem. – Macromol. Chem. Phys., 1988, **189**, (10), 2331–2339.
39. IOAN S., BERCEA M., SIMIONESCU B.C., *Solution properties of ultrahigh molecular weight polymers. 18. Conformational transitions of polystyrene in binary solvents*, Mem. Sci. Sect. Rom. Acad., 1990, **XIII**, 69–75.
40. SIMIONESCU B.C., IOAN S., BERCEA M., SIMIONESCU C.I., *Solution characterization of high-molecular-weight polyacrylonitrile obtained by plasma-induced polymerization*, Eur. Polym. J., 1991, **27**, (6), 553–556.
41. SIMIONESCU B.C., IOAN S., BERCEA M., SIMIONESCU C.I., *Unperturbed dimensions of high-molecular-weight polyacrylonitrile*, Eur. Polym. J., 1991, **27**, (7), 589–591.
42. IOAN S., FLONDOR A., SIMIONESCU B.C., SIMIONESCU C.I., *Solution properties of ultrahigh molecular-weight polymers. 17. Conformational transitions of poly(isobutyl methacrylate) in dilute-solution*, Acta Polym., 1991, **42**, (5), 230–232.
43. IOAN S., BERCEA M., SIMIONESCU B.C., *Flexibility parameter of high molecular weight polymers. 2. Polystyrene in solvent/nonsolvent mixtures*, Rev. Roum. Chim., 1991, **36**, (4-7), 749–755.
44. SIMIONESCU C.I., SIMIONESCU B.C., *On the mechanism of plasma-induced polymerization*, Abstracts of Papers of the American Chemical Society, Apr. 14, 1991, **201**, (2), 304.
45. SIMIONESCU C.I., SIMIONESCU B.C., *The mechanism of plasma-induced polymerization*, Makromol. Chem. – Macromol. Symp., 1992, **54–55**, 595–598.
46. IOAN S., BERCEA M., SIMIONESCU B.C., SIMIONESCU C.I., *Chain conformation and viscometric behaviour of high molecular weight polystyrene in solvent/nonsolvent mixtures*, Polym. Bull., 1991, **26**, 117–122.
47. BERCEA M., IOAN S., SIMIONESCU B.C., SIMIONESCU C.I., *Interpretation of long-chain structure from dilute-solution properties of ultrahigh molecular-weight polymers*, Polym. Bull., 1992, **27**, (5), 571–575.
48. BERCEA M., PEITI C., NAVARD P., SIMIONESCU B.C., *Shear rheology of semidilute poly(methyl methacrylate) solutions*, Macromolecules, 1993, **26**, 7095–7096.
49. SIMIONESCU C.I., CHELARU C., *Sulfonated copolymers of acrylamide synthesized by plasma-initiated copolymerization in order to obtain polymers for enhanced oil-recovery*, Polym. Bull., 1994, **32**, (5–6), 611–616.
50. BERCEA M., PhD Thesis, *Thermodynamic Aspects of Ultrahigh Molecular Weight Polymers in Solution*, Polytechnic Institute of Iasi, Romania, 1994.
51. CONSTANTIN C., SIMIONESCU B.C., *Influence of inter- and intramolecular contacts on the 2nd virial-coefficient*, Eur. Polym. J., 1994, **30**, (9), 1071–1074.
52. BERCEA M., MORARIU S., IOAN S., SIMIONESCU B.C., *On chain flexibility of ultrahigh molecular weight polymethacrylates*, Synth. Polym. J., **1**, (1), 81–87 (1994).

53. SIMIONESCU B.C., IOAN S., IOAN C., SIMIONESCU C.I., *Specific interactions in multicomponent polymer/solvent systems*, Synth. Polym. J., 1994, **1**, (2–3) 23–30.
54. IOAN S., GRIGORESCU G., IOAN C., SIMIONESCU B.C., *Excluded volume effect in polyacrylonitrile solutions*, Polym. Bull., 1994, **33**, 119–125.
55. IOAN S., BERCEA M., IOAN C., SIMIONESCU B.C., *Solution properties of ultrahigh molecular weight polymers. 20. Polymer chain dimensions of poly(methyl methacrylate)*, Eur. Polym. J., 1995, **3**, (1), 85–89.
56. CARAIMAN D., BERCEA M., IOAN S., SIMIONESCU B.C., *Solutions properties of ultrahigh molecular weight polymers. 19. A viscometric study of poly(methyl methacrylate)*, Mem. Sci. Sect. Rom. Acad., 1995, **IV**, (XVIII), 323–330.
57. SIMIONESCU B.C., IOAN C., IOAN S., SIMIONESCU C.I., *Specific interactions in dilute polymer solutions*, Macromol. Chem Phys., Macromol. Symp., 1995, **98**, 1045–1068.
58. BERCEA M., GOSA K., SIMIONESCU B.C., *Ultrahigh molecular weight poly(methyl methacrylate) dilute solutions as studied by UV spectrophotometry and viscometry*, Rev. Roum. Chim., 1995, **40**, (7–8), 661–667.
59. IOAN S., BERCEA M., SIMIONESCU B.C., SIMIONESCU C.I., Chap. *Ultrahigh Molecular Weight Polymers*, in: *The Polymeric Materials Encyclopedia: Synthesis, Properties and Applications*, SALAMONE J.C. (Ed.), Vol. 11. Boca Raton FL: CRC Press, 1996, 8417–8428.
60. BERCEA M., IOAN C., MORARIU S., IOAN S., SIMIONESCU B.C., *Solution properties of ultrahigh molecular weight polymers. 21. Conformational characteristics of poly(methyl methacrylate)*, Polym. Plast. Technol. Eng., 1998, **37**, (3), 285–294.
61. IOAN S., IOAN C., BERCEA M., SIMIONESCU B.C., *Polymolecularity correction factors for the thermodynamic properties of high molecular weight polyacrylonitrile*, J. Macromol. Sci. – Pure Appl. Chem., 1998, **A35**, (4), 609–621.
62. IOAN S., BERCEA M., SIMIONESCU C.I., SIMIONESCU B.C., Chap. *Ultrahigh Molecular Weight Polymers*, in *Concise Polymeric Materials Encyclopedia*, J.C. SALAMONE CRC Press, Boca Raton (Florida), (Ed.), 1998, 1582.
63. CHELARU C., DIACONU I., SIMIONESCU C.I., *Polyacrylamide obtained by plasma-induced polymerization for a possible application in enhanced oil recovery*, Polym. Bull., 1998, **40**, (6), 757–764.
64. BERCEA M., SIMIONESCU B.C., *Rheology of entangled polymer solutions*, Mem. Sci. Sect. Rom. Acad., 1998, **S. IV**, Tome XXI, 122–144.
65. BERCEA M., IOAN C., MORARIU S., IOAN S., SIMIONESCU B.C., *Ultrahigh molecular weight poly(methyl methacrylate) in dilute solution*, Synth. Polym. J., 1998, **5**, (1), 223–231.
66. IOAN C., BERCEA M., VERNET J.-L., SIMIONESCU B.C., *Flow properties of ultrahigh molecular weight poly(methyl methacrylate) in semidilute solutions*, Polym. Plast. Technol. Eng., 1999, **38**, (2), 255–266.
67. Bercea M., Gosa K., Simionescu B.C., *Conformational transitions of high molecular weight poly(methyl methacrylate) in dilute solutions*, Polym. Plast. Technol. Eng., 1999, **38**, (1), 87–97.
68. MORARIU S., BERCEA M., IOAN C., IOAN S., SIMIONESCU B.C., *Conformational characteristics of oligo- and polyacrylonitrile*, Eur. Polym. J., 1999, **35**, (3), 377–383.
69. BERCEA M., MORARIU S., IOAN C., IOAN S., SIMIONESCU B.C., *Viscometric study of extremely dilute polyacrylonitrile solutions*, Eur. Polym. J., 1999, **35**, (11), 2019–2024.
70. IOAN S., BERCEA M., MORARIU S., *Effect of chain ends and chain stiffness on the solution properties of polyacrylonitrile*, Rev. Roum. Chim., 2000, **45**, (7-8), 717–724.
71. IOAN C., BERCEA M., VERNET J.-L., SIMIONESCU B.C., *Dynamic behavior of ultrahigh molecular weight poly(methyl methacrylate) in semidilute solutions*, Macromolecul. Symp., Rheol. Polym. Syst., 2000, **158**, 169–182.
72. BERCEA M., SIMIONESCU B.C., *Rheology of very high molecular weight poly(methyl methacrylate) solutions*, Rev. Roum. Chim., 2002, **47**, (1–2), 155–164.
73. IOAN S., BERCEA M., *Second virial coefficient of oligo- and polyacrylonitrile*, Polymer Testing, **21**, (2), 233–239 (2002)

74. BERCEA M., IOAN S., MORARIU S., *Oligo- and polyacrylonitrile in dilute solution. Excluded volume effect*, Polym. Plast. Technol. Eng., 2004, **43**, (2), 477–490.
75. YAMAKAWA H., *Modern Theory of Polymer Solutions*. New York: Harper and Row, 1971.
76. DOUGLAS J.F., FREED K.F., *Renormalization and the 2-parameter theory. 1*. Macromolecules, 1984, **17**, (11), 2344–2354.
77. DOUGLAS J.F., FREED K.F., *Renormalization and the 2-parameter theory. 2. Comparison with experiment and other 2-parameter theories*, Macromolecules, 1985, **18**, (2), 201–211.
78. DOI M., EDWARDS S.F., *The Theory of Polymer Dynamics*, Clarendon Press, Oxford, 1986.
79. BERCEA M., NAVARD P., *Comparison of elasticity contributions during the flow of a cellulose derivative solution*, Cell. Chem. Technol., 2016, **50**, (5), 601–607.
80. DE GENNES P., *Scaling Concepts in Polymer Physics*, Cornell University Press, 1979.
81. MEAD D.W., LARSON R.G., DOI M., *A molecular theory for fast flows of entangled polymers*, Macromolecules, 1998, **31**, 7895–7914.
82. LARSON R.G., *The Structure and Rheology of Complex Fluids*, OUP, USA, 1999.
83. MEAD D.W., *Development of the 'binary interaction' theory for entangled polydisperse linear polymers*, Rheol. Acta, 2007, **46**, 369–395.
84. MEAD D.W., *Derivation of the 'switch function' in the Mead-Larson-Doi theory*, Rheol. Acta, 2011, **50**, 631–643.
85. LARSON R.G., BRENNER H., *Constitutive Equations for Polymer Melts and Solutions*. Butterworths Series in Chemical Engineering, 2013.
86. CATES M.E., MCLEISH T.C.B., MARRUCCI G., *The rheology of entangled polymers at very high shear rates*, Europhys Lett. 1993, **21**, (4) 451–456.
87. BAICK I.H., YANG W.J., AHN Y.G., SONG K.H., CHOI K.Y., *Structure and properties of ultra-high molecular weight bisphenol A polycarbonate synthesized by solid-state polymerization in amorphous microlayers*, J. Appl. Polym. Sci., 2015, **132**, (10), 41609.
88. MAPAS J.K.D., THOMAY T., CARTWRIGHT A.N., ILAVSKY J., RZAYEV J., *Ultra-high molecular weight linear block copolymers: Rapid access by reversible-deactivation radical polymerization and self-assembly into large domain nanostructures*, Macromolecules, 2016, **49**, (10), 3733–3738.
89. CARMEAN R.N., BECKER T.E., SIMS M.B., SUMERLIN B.S. *Ultra-high molecular weights via aqueous reversible-deactivation radical polymerization*, Chem., 2017, **2**, 93–101.
90. DAO V.H., CAMERON N.R., SAITO K., *Synthesis of ultra-high molecular weight ABA triblock copolymers via aqueous RAFT-mediated gel polymerisation, end group modifications and chain coupling*, Polym. Chem., 2017, **8**, (44), 6834–6843.
91. BAI Y., HE J., ZHANG Y., *Ultra-high-molecular-weight polymers produced by the "immortal" phosphine-based catalyst system*, Angew. Chem. Internat. Ed., 2018, **57**, (52) 17230–17234.
92. YUAN J., ZHANG Y., LI Z., WANG Y., LU H., *A S-Sn Lewis pair-mediated ring-opening polymerization of α -amino acid N-carboxyanhydrides: Fast kinetics, high molecular weight, and facile bioconjugation*, ACS Macro. Lett., 2018, **7**, 892–897.
93. NOMURA K., PENGBOBOL S., APISUK W., *Synthesis of ultrahigh molecular weight polymers with low PDIs by polymerizations of 1-decene, 1-dodecene, and 1-tetradecene by Cp*TiMe₂(O-2,6-ⁱPr₂C₆H₃)-borate catalyst*, Molecules, 2019, **24**, 1634.
94. WU X.H., WANG D.Z., ZHANG S.Y., CAI W.J., YIN Y.X., *Investigation of adsorption behaviors of Cu(II), Pb(II), and Cd(II) from water onto the high molecular weight poly(arylene ether sulfone) with pendant carboxyl groups*, J. Appl. Polym. Sci., 2015, **132**, (20), 41984.
95. DHUWE A., KLARA A., SULLIVAN J., LEE J., CUMMINGS S., BECKMAN E., ENICK R., PERRY R., *Assessment of solubility and viscosity of ultra-high molecular weight polymeric thickeners in ethane, propane and butane for miscible EOR*, J. Petrol. Sci. Eng., 2016, **145**, 266–278.
96. DIMITRIU S., *Polysaccharides: Structural Diversity and Functional Versatility*, Second Edition, CRC Press, 2004.