PETRU PONI

PETRU PONI Institute of Macromolecular Chemistry
of Romanian Academy
41-A, Grigore Ghica Vodă Alley, 700487 Iaşi, Romania

ACADEMIA ROMÂNĂ
SCOSAAR

HABILITATION THESIS

COMPLEX FLUIDS

from thermodynamic and rheological approaches
to the design of new polymeric materials

Author: CS I Dr. Ing. Maria BERCEA

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ABSTRACT

The habilitation thesis **Complex Fluids** *– from thermodynamic and rheological approaches to the design of new polymeric materials* presents a selection of the results obtained after defending the PhD thesis (8 April 1994). The work is organized in three main parts, as follows.

Introduction

General considerations concerning the basic concepts governing the behaviour of macromolecules are very briefly given. The knowledge acquired during the PhD thesis preparation in thermodynamic area and rheology of polymer solutions was further applied to a deeper understanding of the macromolecular behaviour in a variety of conditions and, then, to elaborate new (bio)materials for targeted applications.

The research activity was concentrated mainly in the following areas:

- **thermodynamics of (co)polymer solutions;**
- **rheology of complex fluids;**
- **design and characterization of polymeric (bio)materials.**

The present work resumes the fundamental concepts which were the basis in evolution and development of my scientific carrier and which will be further taken into consideration for the future research activities.

Section I. Scientific achievements

The main scientific interest over the last 23 years was focused on theoretical and experimental investigations in the field of thermodynamics and rheology of polymers.

1. Towards a deeper understanding of the macromolecular thermodynamics in dilute solutions

The actual progress of macromolecular chemistry would not have been possible without a profound knowledge of the behaviour of isolated macromolecular coils surrounded by small molecules of solvent. Thus, the thermodynamic investigations of polymer solutions represented a continuous challenge in my research activity for a deeper understanding of macromolecular behaviour in different environmental conditions (solvent and temperature). Different polymeric systems were investigated: synthetic (co)polymers of different flexibilities in good and theta solvents, polyelectrolytes, polysaccharides, polymer mixtures, and new excluded volume concepts or phenomenological relationships were applied for a better description of the behaviour of polymer coils in dilute solutions.

2. New thermodynamic concepts applied to polymeric systems

An important part of investigations was focused on the dependence of the Flory-Huggins interaction parameter on polymer concentration for various polymer systems in different thermodynamic conditions (solvent and temperature). The new concept of chain connectivity and conformational variability, approach introduced **by Prof. Bernhard A. Wolf** (Institut für Physikalische Chemie, Johannes Gutenberg Universität Mainz, Germany), has proven to be a very useful tool for characterizing the thermodynamic behaviour of polymers in solution. Some representative systems were selected for discussion and the main conclusions are briefly given. A series of unexplainable anomalous phenomena, such as uncommon molecular weight dependence of second osmotic virial coefficient or the existence of multiple critical points, cosolvency or cononsolvency can be realistic explained by taking into account the composition dependence of the Flory–Huggins interaction parameters and the incorporation of the Hitherto neglected features into the theoretical treatment. For polymer/polymer/solvent systems, the use of binary and ternary interaction parameters is required.

3. Polymeric materials: relationships between the structure at different levels and their rheological features

Rheological investigations provide useful information which, correlated with the thermodynamic parameters, allow the design of materials for targeted applications. The flow behaviour was investigated in different shear conditions for many polymeric systems: solutions, suspensions, nanocomposites, (hydro)gels, self-assembling systems, etc. Some results were already published, others were used for the research projects and many aspects are under study. In this work, two model systems are discussed: (i) hydroxypropylcellulose solutions - for illustrating the origin of elasticity; (ii) cellulose whiskers - for evidencing the influence of structure at different levels on the flow properties. These studies were made in collaboration with **Prof. Patrick Navard** (CEMEF Sophia-Antipolis, Mines ParisTech, France).

Stimuli-responsive materials based on synthetic, semi-synthetic or natural polymers, able to go reversibly through a phase transition within a certain range of thermodynamic parameters (solvent quality, temperature) composition, pH, or other environmental conditions, are now of high scientific and practical interest. Small changes in these parameters cause significant variations (infinite at the critical point) in the physico-chemical properties of the individual macromolecules (solubility, structure, shape, size) and their entangled solutions or networks (stability, viscoelasticity, swelling).

The physical and/or chemical gelation was investigated in detail for different polymeric systems and some results are briefly presented in this thesis. Of particular interest are the biomaterials and a few original contributions were reported in this field. Mainly, PVA based materials with versatile and tailorable properties were designed and the structure-relationships were investigated. By using the rheological concepts, other polymeric systems, such as polymer solutions, suspensions, gels and hybrid materials were extensively investigated and part of these results were published in prestigious journals.

During the last 23 years, I was permanently involved in different national (more than 25) and international (12) research projects as project leader or member in the research team. Also, I have also completed post-doctoral fellowships (22 stages, approx. 5 years in total) in France and Germany, where I have improved my professional background and I have initiated new scientific collaborations.

The main original results obtained this period were included in **128 scientific papers** published as coauthor in journals indexed by Web of Science – **122 papers belong to the research area declared in this thesis** – **11 chapters** in books published abroad, **2 books**, and more than **100 participations** at national and international scientific meetings.

The impact of the original research results was recognized at international level by more than 600 citations of the papers (excluding the self-citations) in international journals, by mentioning these priorities in plenary conferences (IUPAC - Prague 1999, Polymeric Materials - Halle 2006, ACS – Anaheim 2011, Makromolekulares Kolloquium - Freiburg 2011, Material Sciences and Technology – Chengdu, China 2017, etc.), in different books, reviews or PhD thesis elaborated in prestigious Universities.

Awards: 1995 –″Nicolae Teclu″ Prize accorded by Romanian Academy of Science;
2009 –″Emilian Bratu″ Medal accorded by Romanian Chemical Society.

Section II. Future research directions: Challenges and actual possibilities

The perspectives and future developments of the research activities, involving PhD students, are briefly presented. Challenges and actual possibilities, the context of the research activities are also discussed. The following directions will be the basis for the next theoretical and experimental approaches:

- **New theoretical and experimental studies in the field of thermodynamics;**
- **Flow behaviour of polymer based systems;**
- **Stimuli-responsive macromolecular systems for designing new polymeric (bio)materials.**

The improvement of the research standards will be promoted in order to maintain the *excellence and academic features* respecting the ethical rules, based on a hard work for a deep knowledge of macromolecular behaviour, also on dynamism, creativity, competitiveness and fair-play.