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Review of the doctoral thesis of Airit Agasty
titled "Scaling model for macroscopic viscosity analysis of polymer solutions"
prepared at Institute of Physical Chemistry PAS
under supervision of Professor Robert Hołyst PhD., D.Sc.

The review was prepared based on a letter (signature SRN. 431.2.2021) sent to my attention by professor Jacek Gregorowicz - the Deputy Director of Scientific Affairs of Institute of Physical Chemistry PAS on 13th of June 2021.

1. Scope and significance of the thesis.

The thesis of Airit Agasty is related to the subject of polymers rheology during their processing. The subject is crucial for the polymer processing industry. The flow of molten polymer or polymer solutions affects the internal structure and properties of the final product. Therefore, the possibility of precise control over the flow of polymer solutions or melts allows designing products with desired properties. Nowadays, there is a growing demand for developing tools and methods for this purpose.

In his work Airit Agasty has concentrated on the studies of polymer solutions. Polymer solutions are less commonly used in the industry than polymer melts, mainly due to the safety requirements. However, there are known some processing techniques in which polymer solutions are applied, such as electrospinning, spin-coating, bonding or 3D printing. Therefore, the knowledge about the rheology of polymer solutions is crucial in such applications. Polymer solutions are complex liquids that require advanced models for characterisation of their structure-property relationships. The internal structure of the polymer solutions affects its viscosity determining materials processing parameters. The viscosity of polymer solutions depends on the flow length-scale and is studied at different levels from nano to macroscale. The higher the internal friction of a fluid, the more resistance it provides to any deforming forces, and the higher is the viscosity of the given fluid. The study of viscosity for polymer solutions usually requires certain scaling laws. Several theoretical models have been developed over the years that predict the viscosity of polymer solutions, including a wide variety of macroscopic viscosity scaling models. However, none is useful across the wide range of concentrations, temperatures, molecular weights and other processing variables. Developed so far scaling models are focused mainly on one aspect or the other in terms of the number of variables they described.

In the presented PhD thesis Airit Agasty has focused on the polymer solutions exhibiting Newtonian viscosity flow. The core idea of this thesis was to apply to macroscale analysis the previously developed scaling model from nanoprobe diffusion in different polymer systems. The nanoscale

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diffusion model defined the effective viscosity experienced by those probes as a function of the probe size, the concentration of the system, the molecular weight of the polymers, and the temperature of the surroundings.

Although the thermodynamics of polymer solutions is well understood, polymer rheology is not. Developing well-defined scaling models that describe polymer solutions appropriately is still a big challenge, therefore undertaking new research in this area is justified. The research topic undertaken by Airit Agasty is an extension of previous work carried out by Professor Hołyst, who performed extensive studies for the nanoscale motion of small probes in complex systems.

The scope of the doctoral dissertation and proposed approaches are relevant to the current trends and challenges in the field of polymer solutions processing.

2. Form and content.

The doctoral dissertation has been prepared as a monograph containing 6 chapters presented concisely on 75 pages with 38 figures and 7 tables.

The structure of the thesis is typical for doctoral dissertations. It contains: (i) an abstract, (ii) introduction with a description of the state-of-the art about the rheology of polymers, the effect of polymer motion on its viscosity, scaling models and finally, the objective of the thesis, (iii) experimental methodology, (iv) development of a universal macroviscosity scaling model and description of crucial scaling model parameters, (v) results of experiments, (vi) analysis of equations for polymer solutions macroscopic viscosity, (vii) summary and overall conclusions, (vii) bibliography based on 144 positions. The number of analysed publications is not extensive. In addition, most publications are over 20 years old. Only 13 publications are from the last 5 years, including one self-citation. The doctoral dissertation also contains a list of figures, tables, abbreviations, physical constants and symbols.

The overall quality of the dissertation is good. The style and English language are satisfactory, however it is not clear why the plural is used in the description of the Ph.D. Candidate's achievements e.g. "we expanded", "we required", "we used", "our goal", "our experiments", "our characterisation method", etc.

3. Scientific content and research methodology.

The core idea of this thesis was to apply to macroscale analysis the previously obtained scaling model from nanoprobe diffusion in different polymer systems, such as: polydimethylsiloxane (PDMS) in ethyl acetate, hydroxypropyl cellulose (HPC) in water, polymethylmethacrylate (PMMA) in toluene, and polyacrylonitrile (PAN) in dimethyl sulfoxide (DMSO). Four different systems were selected with polymers varying in their polydispersity. The nanoscale diffusion model defined the effective viscosity experienced by those probes as a function of: (i) the probe size, (ii) the concentration of the system, (iii) the molecular weight of the polymers, and (iv) the temperature of the surroundings. In this work, the same model was expanded to macroscale analysis of viscosity by applying it to different polymer systems. The goal was to use ~~the~~ effective viscosity to derive the macroscopic viscosity.

The novelty of research work is clearly presented in the light of existing state-of-the-art solutions described in Chapter I. Although extensive studies were performed on nano-objects and colloids using a length-scale dependent viscosity model, not a lot of studies were made to cover the macroscopic viscosity for complex systems. Rheology of polymer solutions suffers from the lack of a model of viscosity applicable across a wide range of concentrations, temperatures, molecular weights, and other processing variables. Previous scaling models lacked in one aspect or the other in terms of the number of variables they described.

The experimental part of the dissertation is presented in Chapter 2, which describes the experimental methodology, and in Chapter 4, which presents the measurement results. The experiments cover the measurements of: (i) viscosity using a rheometer for a wide range of polymer concentrations at different temperatures, (ii) hydrodynamic radii by dynamic light scattering (DLS), (iii) molecular weight distributions and polydispersity index by gel permeation chromatography (GPC). Such measurements were crucial to obtain the data required for application and fitting with the previous nanoprobe diffusion model.

Finally, it was possible to obtain the length-scale dependent viscosity scaling model. The development of a universal macroviscosity scaling model was described in details in Chapter 3. A few critical parameters were appropriately identified to construct a scaling model for the viscosity of polymer solutions, such as hydrodynamic radius, gyration radius, correlation length, concentration, and activation energy. The selected parameters were analysed in the context of macroscopic viscosity for polymer solutions in Chapter 5. The Chapter 5 is crucial for the scaling model for macroscopic viscosity analysis of polymer solutions. Results of relative viscosity measurements were analysed as a function of the ratio of concentration to overlap concentration, as well as average molecular mass. The dilute, semi-dilute concentration regions were identified for all investigated polymer solutions and additionally concentrated region only for PDMS-ethyl acetate. The investigation and modification of all different model parameters for polymer solution systems were carried out. Developed scaling provides a method for characterising the macroscale viscosity of polymer solutions. It is applicable for a broad range of concentrations, molecular weights, temperatures and polydispersities.

The Ph.D. Candidate's main achievements consist of extending the scaling model to cover concentrations from dilute to concentrated solutions. He obtained relations between the coil dimensions as a function of concentrations, explained its applicability for selected polymers with diverse molecular weight distributions, clarified the reasons and means for the validity of this model regardless of the polydispersity of the polymer samples and provided final consolidated information about all the different parameters in models. The studies involved measurable parameters, not the fitted parameters. Conclusions were drawn after performing precise viscosity measurements through accurate techniques for several good solvent systems. The developed model can be used to analyse and characterise polymer solutions for all purposes. Unfortunately, it cannot be directly applicable for polymer melts, which are more commonly used in the polymer processing than polymer solutions. So the developed model has limited application in the industry.

Taking into account the high scientific quality and a large number of performed research tasks, the reviewed dissertation fulfils the expectation of a doctoral thesis. The Ph.D. Candidate demonstrated how the knowledge about the rheology of the polymers could be applied to develop valuable tools for a large number of commercially available polymer solutions used in practice. The methodological approaches applied in the research tasks are following scientific standards. The methods used to characterise polymer solutions are properly designed and performed. The results are critically discussed and compared to the already published data. The novelty and significance of the achieved results and the way they are obtained indicate that the thesis outcomes might be published in prestigious international journals. The first paper has already been published in Polymer (IF 4.430).

4. Remarks.

While reading the doctoral dissertation, a few questions and comments have arisen, which do not affect the value and quality of the presented dissertation, but need further discussion or explanation.

1. The question arises about the materials chosen for the investigations. What are the examples of their practical applications and methods used for their processing?
2. It is not clear what the Author means by "normal operating range for most everyday polymer products" (page 22). Some examples should be provided.
3. I cannot agree that "It is conventional to measure the viscosity at all polymer processing industries…." (page 22), because in the industry, the most often measured processing parameters are Melting Flow Rate (MFR) or Melting Flow Index (MFI).
4. Are the Figs. 1.1, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, shown in the Chapter I, the authorship of PhD Candidate?
5. Fig. 4.6 should be placed in Chapter 4.3, not in 4.2.
6. Figs. 4.6 and 4.7 show the results of GPS and DLS measurements, respectively, but only for PDMS. The measurements were also performed for HPC, PAN and PMMA, but the results are not shown. Why?
7. The viscosity was measured in the range of 283-303K. What was the reason for such temperatures selection?
8. In equation 5.6, in the case of PDMS, the applied v value was 0.53 instead of 0.6. The question arises of how v was estimated.

5. Conclusions.

In view of the results achieved, I consider that Airit Agasty doctoral thesis titled "Scaling model for macroscopic viscosity analysis of polymer solutions" submitted for the review fulfils the requirements for doctoral dissertation under the Act on Scientific Degrees and Scientific Title (Article 187 of the Act of 20 July 2018. Law on higher education and science Dz.U. 2018, item 1668, as amended). Therefore I recommend the dissertation to be accepted and PhD Candidate Airit Agasty to be admitted to further stages of the doctoral thesis and to the public defence at the Institute of Physical Chemistry of Polish Academy of Science.

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