

Gliwice, 08.07.2021 r.

REVIEW OF PhD THESIS OF M.Sc. AIRIT AGASTY
“Scaling model for macroscopic viscosity analysis of polymer solutions”
the work done at the Institute of Physical Chemistry,
Polish Academy of Sciences, in Warsaw
under the supervision of prof. dr hab. Robert Hołyst

Scientific development is a determinant of progress, and at the same time aims to popularize and simplify materials and their characterization techniques. The history of polymers shows some repeatability in improving what is already available to increase the variety of properties and range of applications. At the beginning, the first synthetic polymers were introduced to the market, imitating nature and increasing the scale of production, then the interest in miniaturization and nanotechnology provided the highly specialized materials. These changes are strongly related to the progress of the methodology, thanks to which the research can be performed both in the nano- and macroscale, but it requires appropriate modification of the concept to give it the second life and become the actual topic for science and industry. If such redesigned concepts become available for a wide range of polymers, irrespective of their properties, and at any scale, this saves time, which also has an economic dimension. regardless of their properties and on any scale, it allows to save time, which also has an economic dimension.

The issues taken in the doctoral dissertation of MSc Airit Agasty include the search for a universal physicochemical model that would enable macroscale analysis of viscosity as a polymer characterization technique for industrial applications. For this purpose, the PhD Student used the equation for the macroscopic viscosity previously developed for the solutions of polyethylene glycol, to extend the range of the systems by 4 different polymers with various molecular weights and dispersity indices.

The dissertation has nonstandard composition. It contains general information, such as declaration of authorship, funding sources, abstract, acknowledgements, list of publications, list of figures, list of tables, list of abbreviations, physical constants, and list of symbols. In the main part there is Chapter 1: Introduction (p.1-22), Chapter 2: Experimental methodology (p.23-27), Chapter 3: Development of a universal macroviscosity scaling model (p.29-34), Chapter 4: Experimental conditions and results (p.35-40), Chapter 5: Macroscopic viscosity analysis for polymer solutions (p.41-62), and Chapter 6: Summary and conclusions (p.63-65). Bibliography is the last chapter (p.67-75) listing 144 references, where 72% of articles has

been published before 2000, including 31% of the older ones before 1970, which means that studies refer to issues that were of particular interest in those years. On the other hand, the development of the methodology allows for a better understanding of what justifies the subject matter.

In Chapter 1 the Author presents fundamentals of polymers, including their classification on elastomers and plastomers. Next, He focused on rheology describing fluids behavior and viscosity studies with generalized Newtonian fluid models for non-Newtonian fluids. There is a several scaling concepts, which are helpful to understand the statics and dynamics of polymeric chains in the solution, and in the melting state. The macromolecules depending on concentration demonstrate various degree of entanglements, whereas those above critical concentration forming physical networks show different swelling degree due to blob size identified as a chain length and coil density. The polymer motion in solution has been described by numerous models, for example that of Rouse and Zimm, Doi and Edwards, Kirkwood-Riseman to show the viscosity influence. However, there was still a problem to use these calculations for full range of concentration, and to reach the results with expected accuracy. Because of that the macroscopic viscosity scaling models have been developed, what is reported in literature by numerous scientists, such as Huggins, Baker, Arrhenius, Martin, Flory, and etc. One the popular equations describing the relationship between intrinsic viscosity and molecular weight has been provided by Mark and Houwink in 40's. The extensive studies on viscosity have applied a various other physicochemical parameters, e.g. countour length, static stiffness, activation energy, but these concepts were limited to dilute or semi-dilute solutions, and could not be applied as a different length-scales models. The viscosity has been also investigated in nanoscale by monitoring diffusion effect in complex fluids with hierarchical structures and the heterogeneous materials in physical and biological systems. It is worth to highlight that the nanoviscosity issues have been advanced by the group of prof. Hołyst, who have developed equation based on the Stokes-Sutherland-Einstein equation indicating the correlation of diffusion coefficient, which is inversely proportional to viscosity and nanoparticle radius. Additionally, transport properties of complex liquids indicated deviation from the above equation as the specific length-scale dependence (growing with reducing ratio of radius to gyration radius), which resulted another equation, where the effective viscosity was exponential function of effective particle size, energy of activation, and correlation length related to the gyration radius and the crossover concentration. This nanoscale model has been tested on macroscale systems of polyethylene glycol solutions in water.

The next 3 chapters are devoted experimental part containing: the equipment used for measurements by viscometry (rheometers), dynamic light scattering (DLS), and gel permission chromatography (GPC) (Chapter 2), characteristics of viscosity model and the

main parameters (Chapter 3), polymer systems used in studies and measurement conditions of viscosity, molecular weight, and hydrodynamic radius (Chapter 4).

The obtained results are discussed in Chapter 5, which starts from the basic equation for the effective viscosity called in further part of thesis as macroscopic viscosity due to the large sizes of polymer particles. There is also reminding of its limitations for some ranges of concentration, molecular weight, and temperature. The application of this model required to calculate the critical concentration (c^*) at transition of dilute to semi-dilute solution for the studied systems of HPC/water, PDMS/ethyl acetate, PAN/DMSO, PMMA/toluene. Then it was used to plot the semilogarithmic dependence of the measured viscosity as function of the c/c^* ratio. In the case of PDMS (28k) system the second crossover point was detected as the transition to concentrated solution (c^{**}). The results for initial scaling of viscosity at fixed the second crossover concentration c^{**} and the scaling parameter a were similar to that obtained at fixed the first crossover concentration c^* , although their linearity was improved. The ratio of hydrodynamic radius to gyration radius, which is related to changes of coil dimensions with concentration variation, indicated similar behavior for the studied systems in dilute solutions. However it was slightly higher for PDMS in semi-dilute range, which let to determine the relationship for prediction of exponent r at parameter x defined as the mole fraction of the polymer in the solution. According to further assumption for the concentrated solution the Author postulate the polymer coils should shrink due to domination of attractive interactions between chains, resulting the reduced value of R_h/R_g ratio. The calculated scaling parameter a has the highest value above 1 in dilute solution, what is typical for inflexible spheres, and then it was reduced with the increase in polymer concentration. Additionally, the flow process connected with overcoming the barriers during macromolecule motion can be described by the activation energy, which includes the total interactions between polymer and solvent. Similar results were obtained for all systems, although the size of monomeric units in HPC are larger 7-8 times than those in the other studied polymers, which was explained by limited solubility of semi-flexible chains with tendency to crystallization. Another important parameters, such as molecular weight and dispersity of polymer, were verified by the viscosity scaling model with good fitting and linear dependence. Generally, the results of monodisperse vs polydisperse polymers did not emphasize influence, but above the certain level of polydispersity it is more precise option. Similarly, linear fitting was resulted using M_w for the viscosity scaling calculations ($R^2=0.9976$), but it was slightly improved replacing M_w by M_v ($R^2=0.9985$). Finally, applying all scaling parameters, which were assumed and estimated before to simplify the proposed model, were successfully verified.

The research presentation and the results interpretation do not raise any substantive objections, although they require some additional explanation:

- 1) Why exponent r for PAN is higher than it could be expected because the polymer is characterized by the chain stiffness is caused by double bonds in the main chain?
 - 2) The values of R_g and R_h are not presented. The same the literature references, from which the values of similar polymer-solvent systems (similar does not mean the same) were used for R_g calculations, should be given.
 - 3) The correlation indices R^2 are valuable confirmation for the well-fitting dependency and it is useful for comparison, but these values are provided just for fig. 5.9 and 5.13.
 - 4) Polymerization techniques listed in Chapter 1.1 should be completed by polymerization in bulk, which is applied very often in industry. Additionally, the presented classification of polymers in aspect of physical properties related to T_g parameter contains elastomers and plastomers, which differs with the type of rheological deformation, and the fibers, what is not understandable because these are a kind of materials based on the processed polymers, similarly for example foils.
 - 5) Please, explain how parameter m defined as the mass of the polymer in the solution is connected with eq. 1.8? Similarly, how eq. 1.28 describes two cross-over points c^* and c^{**} ?
 - 6) What is the key for selection of the following systems for the investigations? Why does this list not include polystyrene as aromatic representative or poly(vinyl chloride) as representative of fluoropolymers, which are common industrial polymers with different physicochemical properties? Additionally, the verification of polymer in two different solvents would be interesting in the further studies on the viscosity model.
- In conclusions, it is mentioned about not direct application of the scaling model for polymer melts and two new equations appear, but previously these results were not discussed.
- 7) The final sentence stating that the studied length-scale characterization method is uniformed “for different types of polymer systems...” seems to be overinterpretation due to just 5 polymer systems were tested, which needed the fitting parameters. However, these values might not be the well-fitted for the other polymer systems. What are the disadvantages of this method?

Generally, the dissertation is well written with some small language mistakes, although the Author did not manage to avoid the other errors, such as: unexplained abbreviations (e.g., MHS); different abbreviations for the same issues (D,S,C vs Dil, SDL, Conc); missing units (e.g., p.15); the interchangeable use of the terms molar mass vs molecular weight; unfortunate wording (e.g. p.1 orientation instead topology/architecture); not correct numbers of figures in the text (e.g. p.49 eq. 5.14, but should be 5.9, p.50 eqs. 5.8-5-16?); presentation of some equations and figures more than one time, but with different numbers; not unified bibliography data for references.

The research work described by Mr Agasty required analytical skills and theoretical knowledge in area of physicochemical chemistry to get a several scaling parameters and check the viscosity scaling model applicability. It was performed within the M. Skłodowska-Curie grant of the European Union Horizon 2020 co-financed by the Polish Ministry of Science and Higher Education as well as within the Maestro grant founded by the Polish National Science Center. His scientific achievement includes 3 articles published in the years 2020-2021 in international journals from the JCR list (IF: 1.195-4.723), where he is the first author in two of them related to the PhD thesis. It means that the criterion of scientific novelty documented by articles is achieved as well as the obtained results has influence on the development of physical chemistry of polymers.

Taking above into account, I conclude that the presented doctoral dissertation meets the requirements set out in Art. 187 of the Act of July 20, 2018 Law on higher education and science (Journal of Laws of 2018, item 1668, as amended). Therefore, I am applying for admission of Mr Airt Agasty to further stages of the doctoral proceeding.

