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OPINION

on Doctoral Thesis *Scaling model for macroscopic viscosity analysis of polymer solutions,* by Mr. Airit Agasty.

In recent decades we have been facing fast development of materials and materials technologies. Especially rapid development has been observed in the fields of electronic and polymeric materials. The latter group of materials brought undoubtful revolutionary changes to structural and functional applications and opened almost unlimited opportunities before engineers. However, recently the overwhelming domination of plastics in the world became also a nightmare for ecologists.

Development of new materials and prediction of their performance during processing can be done experimentally or by using modelling and computer simulation technique. The latter method is efficient, cost effective and much more environmentally friendly. Mr. Airit Agasty focused his research on development of scaling model for prediction of the viscosity changes of polymers on a basis of simple measurements of their macroscopic parameters. The research work carried out by Mr. Airit Agasty has both scientific and technological aspects. The practical part is related to the possibility of control over the flow of polymer solution in industrial processing.

The thesis has a standard form, starting with theoretical introduction, comprising fundamental information on the polymer structure and rheology. This part contains also characteristics of Newtonian fluids, definitions of viscosity, shear rate and shear flow. An important part of the introduction is devoted to the viscosity studies and the roles of the length and time scales for the proper description of the polymer flow. From these considerations arises the necessity of scaling the models what makes the major idea of the thesis. The Author discusses factors that change with the length scale such as: individual coil statics, occurrence of coil swelling and entanglement of the chains and molecular weight exponent of the viscosity, which the Candidate indicates as crucial for polymer scaling. Furthermore, the Author presents most relevant, existing, theoretical models for prediction of the viscosity in polymer solutions. Among them the Author discusses single chain model of Rouse and Zimm, which is regarded as not

feasible for description of the viscosity accurately for long chain polymers. On the other hand, reptation model of Doi and Edwards, regarding polymeric chains as rigid rods, is considered by the Author as inaccurate for polymer solutions with varying parameters. Also, as inaccurate was assessed Extended Kirkwood-Riseman model for viscosity, which requires greater number of terms when concentration of the solution decreases. All the briefly presented models suffer from limitations and require simplifications, which make the modelling inaccurate and distant from reality, especially in terms of universality.
Mr. Airit Agasty undertook also assessment of selected macroscopic viscosity models, including Huggins, Lyons and Tobolsky, Weissberg, Simba, Takahashi and many others, who contributed to their further improvements and developments.
Many efforts have been devoted towards nanoscale viscosity studies. The theoretical studies are supported by the development of innovative experimental techniques including e.g. Fluorescence Correlation Spectroscopy. These problems have been for many years exploited by the research group led by the Author's supervisor.

The state-of-the-art presentation is complete and takes into consideration the most important contemporary findings in the area of viscosity modelling in polymeric systems. This extended review of the most important models forms a sufficient introduction to the own studies and proves their justification. From the literature overview the Author concluded that the available list of existing models suffers from the lack of a model that can be applied for a wide range of concentrations, temperature, molecular mass and other variables. Such a statement enabled also the Author to formulate the objectives of the thesis, which generally are aimed at application of the macroscale analysis to the previously obtained scaling model from nanoprobe diffusion, which defined the effective viscosity measured by those probes as a function of the probe size, concentration of the system, molecular weight of the polymers and temperature.

For the experimental verification of his model the author derived macroscopic viscosity for selected polymer solutions that are commonly used: polydimethylsiloxane (PDMS) in ethyl acetate, hydroxypropyl cellulose (HPC) in water, polymethylmethacrylate (PMMA) in toluene, and polyacrylonitrile (PAN) in dimethyl sulfoxide (DMSO). The experiments comprised measurements of viscosity for a wide range of polymer concentrations at different temperatures, hydrodynamic radii ,measured by dynamic light scattering (DLS), molecular weight distributions and polydispersity index evaluated by gel permeation chromatography (GPC). For the viscosity measurements the Candidate applied rotational rheometer and a viscometer.

Dynamic light scattering method enabled the particle size analysis in the nanometer range and calculation of diffusion coefficients.
Tin this paragraph the Author could have probably avoided detailed description of design and basic principles of operating instructions of various commercial equipment. Nevertheless, the experimental methods chosen, equipment type and applied parameters are appropriate and adequate for providing necessary data for the modelling.

The Author undertook an ambitious and difficult task to further improve the scaling models of viscosity that have been already widely studied and elaborated by many scientists in the world. Somewhat challenging was also the necessity of making a choice of the evaluation and measurement methods, of the required parameters, from a variety of possible procedures.

Chapter 3 is devoted to characteristics of the developed model. In the Author's intention the model should be valid for a range of concentrations, molecular weight, hydrodynamic radius $R_h$, gyration radius $R_g$, correlation length, temperature variations, molecular weight distribution, crossover points, polymer-solvent compatibility and activation energies for the process. Chapter 3, where the characterization of the crucial parameters and their roles in the model are presented is, in some parts, somewhat confusing, because it combines methodology and results together. Moreover, some details of experimental work are not satisfactory clarified. For example, in Tables 3.1 and 3.2, hydrodynamic radius $R_h$ and gyration radius $R_g$, appear. It has not been clearly explained how these radii were calculated, were the solution concentrations taken into account and how the coefficients $K$ and $y$ were fitted. These parameters appear latter in Chapters 4 and 5.4, where the Author mentions that the measured values (Tables 3.1 and 3.2) were combined with literature values. The final values of these radii are however not adequately shown.

Experimental results, together with experimental conditions, are presented in Chapter 4. The rheometric plots of viscosity versus shear rate confirm the assumed Newtonian character of the fluids. Other experimental results comprise viscosity versus concentration, for different temperatures and molecular mass, measurements of molecular mass distribution and hydrodynamic radius.

Development and evolution of the model is presented in Chapter 5. This is the most important part of the thesis. Measurements of the effective viscosity as a function of the probe size, from diffusion coefficients of nanoprobes, enabled the Author to formulate an exponential equation, combining hydrodynamic radius, length scale coefficient and scaling parameter, depicted as 5.4 in the thesis. Further parts of this chapter demonstrate the more accurate approximation of the formulae, leading toward

the linear fitting. The first problems, to be solved, were related to the extension of the concentration to the semi-dilute regime and existence of two crossovers. This was solved by the Candidate through introduction of the overlap concentration coefficients from dilute to semi-dilute $c^*$ and from semi-dilute to concentrated $c^{**}$ regime. Many efforts have been also put by the Author to further understanding of the effect of concentration on the coil dimensions. This was effected by detailed study of the concentration dependence of the hydrodynamic radius parameter $R_h$. Unfortunately, the concentration-size dependence relation was possible to determine for PDMS only, due to the lack of a high concentration regimes for the three other polymeric solutions studied. Consequently better fitting of the $R_h$ parameter was achieved.
Another parameter, taken into account by the Author, was the scaling exponent *a*. On a basis of the literature information the Author was able to formulate appropriate relations and calculate the values for all the four polymers, within diluted and semi-diluted regimes and for PDMS for concentrated area.
The activation energy for motion of the monomers in solvents, has also been thoroughly studied and evaluated in Chapter 5. Finally, the Eyring theory, based on overcoming the molecular layer frictional energies, was adopted in the thesis.
Molecular mass was the next parameter considered as crucial in the model developed. Mr. Airit Agasty chose the method of weight distribution to divide the molecular mass into fractions, such as: weight average molecular mass $M_w$ and viscosity average molar mas $M_v$. An extensive discussion of both parameters on the viscosity prediction has been done in the thesis. Finally, the Author concluded that fitting the viscosity equation with the $M_w$ provides better linearity of the dependence across the various concentration ranges.

The part of the thesis related to presentation ad discussion of the results is very interesting and proves that Mr. Airit Agasty possessed deep knowledge on the processes and phenomena occurring in the polymeric systems. The author shows here the ability of a critical assessment of the vast amount of literature information and selection the most valuable data for his own research. Mr. Airit Agasty proved it for all the polymeric solutions studied. As a consequence of these activity a linear plot of the viscosity versus all the parameters chosen was achieved.

Summary

Mr. Airit Agasty has extended the scaling model to cover concentrations from dilute to concentrated in polymeric solutions for selected systems. He showed relations between the coil dimensions as a function of concentrations and applicability of his model for commercial polymers with different molecular weight distributions. He presented the validity of this model regardless of the polydispersity of the polymer

samples and provided an information about the various parameters of the model. The model presented provides the possibility to use a length-scale based polymer investigation technique based on easily available viscosity measurements. This method is effective for a wide variety of applications in the nanoscale as well as the macroscale.

One has to admit, that although the variety of existing models, discussed in the thesis have may disadvantages, the model proposed by the Candidate is not free from limitations and simplifications either. Assumption of a purely Newtonian character of the polymer solution is a simplification. Moreover, application of the model to diluted polymers substantially limits its industrial exploitation for condensed liquid polymers.

Final conclusion

Concluding, I would like to state that Mr. Airit Agasty has fully completed the planned research program and achieved its aims. The Candidate analyzed the existing viscosity models and formulated his own approach that can be applied across wide range of variable parameters. The thesis contains important results and conclusions, valuable from scientific and application points of view. The Candidate's research has substantially contributed to the development of knowledge of the polymer viscosity behavior under influence of material variables, such as: temperatures, hydrodynamic radii, molecular weight distributions and polydispersity index, for the solution concentrations ranging from dilute to concentrated. Mr. Agasty carried out his research with high inquisitee and accuracy aiming at proper learning and interpreting the phenomena occurring in the polymer's solutions.

I declare that the thesis *Scaling model for macroscopic viscosity analysis of polymer solutions,* submitted by Mr. Airit Agasty fulfills the requirements identified in the Law on Higher Education and Science of 20 July 2018 y., art. 187 (Dz.U. z 2018 r. poz.1668 ze zm.) and recommend it for further processing at the Scientific Board of the Institute of Physical Chemistry, Polish Academy of Sciences.