



# Instytut Fizyki Molekularnej Polskiej Akademii Nauk

Mariana Smoluchowskiego 17, 60-179 Poznań  
tel. 61 8695 276, fax 61 8684-524  
www.ifmpan.poznan.pl  
e-mail: [tretiakov@ifmpan.poznan.pl](mailto:tretiakov@ifmpan.poznan.pl)

Poznań, 03.10.2018

Dr habil. Konstantin V. Tretiakov  
Associate Professor  
Department of Computational Physics of Complex Systems  
Institute of Molecular Physics  
Polish Academy of Sciences

**Review Report on the PhD thesis of Wojciech Radosz**  
entitled  
**"CHARACTERIZATION OF LOCAL STATIC AND DYNAMIC  
PROPERTIES OF POLYMER SYSTEM IN BOND-FLUCTUATION MODEL"**

**Supervisor: prof. dr hab. Antoni C. Mituś**

This thesis contributes to the current knowledge in polymer science. Properties of polymers depend on local structure of polymer system which is crucial for modelling of physical phenomena in model polymer systems and for interpretation of experimental results. This thesis mainly focuses on a study static and dynamic characterization of local structure of typical configurations of model polymer system and of model host-guest systems. Based on simulations of polymer system using lattice bond-fluctuation model, characterization of microscopic distribution of monomers and local voids (local free volume), clusterization of local voids, shape and size of clusters, and times of life of voids has been done. The topic of thesis is modern and relevant in the context of analysis of local (static and dynamic) structure of model polymer systems and the modelling of all-optical poling effect in host-guest system.

Wojciech Radosz's PhD thesis consists of six chapters. The dissertation comprises 73 pages, 43 figures, 21 equations and is prepared very carefully. At the beginning of this dissertation lists of symbols are introduced. The work ends with a bibliography of 54 items, among which there are three publications co-authored by Wojciech Radosz.

The first chapter constitutes a general introduction which contains a brief literature overview and the objective of thesis. The chapter 2 presents the methodology. In my opinion, both the introduction to the subject and the methodological background are too superficial. Taking into account the existing extensive literature on the subject, one might expect a better introduction and more extensive methodology part. All specific comments are pointed out below.

The chapter 3 is devoted to the characterization of the static local structure of bond-fluctuation model (BFM) of polymer system. The Author introduces local void parameter ( $V$ ) and analyzes its properties (maps, histogram, distributions and correlations) and studies clusterization of local voids and the shape of clusters. The Author has found (i) inhomogeneous distribution in space of local voids, (ii) two different types of correlations of voids (liquid-like and single exponential), (iii) power law distribution of sizes of clusters with  $V = 6$ , (iv) quasi 2-dimensional character of clusters with  $V = 6$ , and (v) fractal features of clusters with  $V = 6$ .

In the chapter 4, the Author characterizes the selected dynamical/kinetic properties of bond-fluctuation model of polymer system. In particular, beside of analysis of time dependent properties of local void parameter ( $V$ ) and local mobility parameter ( $C$ ), the Author introduces a new parameter,  $D$ , and uses it for localization of glass transition. It has been found that kinetics of the local free volume,  $V(r,t)$ , changes with the temperature (from frozen-like at low temperature to mobile-like at high temperature). Except that, parameters  $V(r)$  and  $D(r)$  reveal the presence of the glass transition, while parameter  $C(r)$  does not. In my opinion, this is one of the most interesting chapters of the thesis but the presented analysis of dynamic properties is rather in its preliminary stage.

Chapter 5 is devoted to the study of nonlinear optical effect, namely all-optical poling process. Using a simple kinetic Monte Carlo model, the Author studies the kinetics of non-interacting photo-switchable guest molecules (model azo-dye) dispersed at low concentration in a host (model polymer matrix) in the all-optical poling process close to the glass transition temperature. Complex kinetics of guest molecules has been found using analysis of time dependencies of order parameters which were proposed in this thesis. It was found that the most distinct complex kinetics occurred around glass transition temperature.

Summary and general conclusions of the thesis are contained in the Chapter 6. There, the Author highlights the main results of the thesis and at the end of that chapter the Candidate makes recommendations for the future work.

### Critical Remarks and specific comments

There are some remarks and comments that should be explained in details.

- ✓ The present study has been done for polymer system consisting of 24000 polymer chains. Did the Author study other sizes of the system? What effect will the size of the studied system have on the results?
- ✓ An interesting result is the observation of the power law distribution of sizes of clusters with  $V = 6$  (Figure 3.14). Did the author try to interpret this result? Does not the uniqueness ( $V = 6$ ) result from the symmetry of the adopted model (Figure 3.3)? The central cube is surrounded by exactly six other cubes.
- ✓ According to the author, is there any advantage of the D parameter introduced in the doctoral dissertation compared to other parameters?
- ✓ In the page 65, the Author wrote "R is a tunable parameter in experiments". Could he give some typical or approximate values of this parameter in experiment?

### Minor remarks

Page 7: In the List of Symbols, the Author used abbreviations. I think that the format of the doctoral thesis allows one for the use of full names of physical quantities and parameters.

Page 9: It would be good to support with references the following sentence in Outline of the problem: "Different phenomena connected with them give large variety of experiments and possible applications."

Page 14: A rather unfortunate statement on page 50, "Now, by the addition of small random displacement to old configuration we generate new one with ...", should be corrected. I think that one cannot add displacement to configuration.

Page 17: in line 3 there is a typo: instead of "...by Carmesin an Kremer..." it should be "...by Carmesin and Kremer...".

In page 21, the Author wrote "Similar analysis was done for other phases of the simulation (plots not shown here)." Similar statements, namely (plots not shown here) or (not shown here), one can find on pages 26, 27, 29, 34, 60. It is a pity that the Author excluded those plots from dissertation. In my opinion, the format of the doctoral thesis allows one to present also results which sometimes, for the limited volume reasons, could not be included into a regular publication.

In page 28, one can read "It suggests the existence of correlations and clusterization." It is not clear which correlations the author has in mind.

Page 43: in last line, it seems that instead "(Figs. 4.2. and 4.4.)" it should be "(Figs. 4.2. and 4.5.)".

Page 44: In a theoretical work I would expect instead of writing "The fits are reasonable (no further statistical analysis was done)." The Candidate could simply give the value of the coefficient of determination, usually denoted  $R^2$ . Here, there is also a typo: "analysis". It should be "analysis".

Page 49: Missed dot in the last sentence in second paragraph.

Page 50: Second paragraph, maximum occurs for  $2\pi$ .

In description of Figure 5.4: Instead "(right) Normalized angular distribution at  $t = 10^4$  MCS for..." it should be "(right) Normalized angular distribution at  $t = 2 \cdot 10^5$  MCS for..."

Page 59: Second paragraph, Instead of "Fit. 5.13." it should be "Fig. 5.13.".

Figure 5.17: In the description of the figure, symbols in insert of figure are not defined.

The above comments and minor imperfections do not affect my positive evaluation of the entire dissertation. Because I am not a native speaker, I do not take responsibility for assessing the correctness and level of English.

**In my opinion, this thesis contains original and valuable scientific results. The work is innovative and may encourage other researchers to take candidate's ideas forward by themselves. In my opinion, the reviewed thesis fulfills all requirements posed on these aimed for obtaining PhD degree. This thesis is ready to be defended orally, in front of respective committee.**

