Macromol. Symp. ***174***, *393–402 (2001)*

Structure and Properties of Single Complex Macromolecules and of Related Bulk Systems

Tadeusz Pakula

Max-Planck-Institute for Polymer Research, P.O. Box 3148, 55021 Mainz, Germany* and Department of Molecular Physics, Polytechnic of Lodz, Poland

SUMMARY: Structure and dynamics of complex macromolecules in computer simulated systems is analyzed. The algorithm based on cooperative molecular rearrangements is applied to various macromolecular structures represented in a simplified form on the lattice. Various macromolecular architectures such as linear chains, stars, dendrimers, bottle-brush polymers as well as cyclic chains and catenane are considered both as single molecules and as dense systems corresponding to polymer melts. A broad range of structural parameters characteristic for each system is taken into account. In some cases, the simulation results are compared with the behavior of real systems in which the structure and dynamics has been studied by X-ray scattering and mechanical spectroscopy, respectively.

Introduction

A variety of macromolecules with intramolecular architectures differing by topology of bond skeletons and by the distribution of monomers of different type can now be synthesized [1-4]. In many cases, they constitute self-assembling systems which generally can be regarded as complex fluids in which various kinds of interactions and a predetermined atomic order within molecules involve a supramolecular order. By a specific molecular design of the atomic constitution and by variation of the topology of bond skeletons of macromolecules, contributions of various interactions can be controlled to a large extend. The macromolecules have usually sizes within the nanometer range. Recent experimental techniques still have considerable limitations in a precise determination of structure and dynamics within objects of these sizes. Properties of bulk systems with such molecules can, therefore, not always be uniquely related to the molecular details. On the other hand, various complex molecular structures can easily be generated by a computer and using appropriate simulation algorithms their structure and dynamics can be studied [5-8]. Single macromolecules diluted in a good solvent have different dimensions and different dynamics than in a melt where they are surrounded by other macromolecules. Therefore, it is interesting to consider both the behavior of single macromolecules and the behavior of dense systems corresponding to bulk materials.

CCC 1022-1360/00/$ 17.50+.50/0

Examples of results based on both simulation and experimental studies obtained recently for such macromolecules are here presented and discussed.

Simulation Method

The methods used are based on cooperative rearrangements in lattice macromolecular systems and are known as the cooperative motion algorithm (CMA) [e.g. 5] and the dynamic lattice liquid model (DLL) [9,10]. They have recently been applied to simulate catenanes [11], multiarm stars [6,12,13], dendrimers, bottle brush molecules [5,14] and microgels [15]. However, the methods have been described in various places in the literature, it is important to stress here their unique properties which made them very effective for studies of molecular and macromolecular systems within the size scale corresponding to the nanometer range. In these simulation methods, the molecules are represented by assemblies of beads (representing monomers) connected by non breakable bonds in a way corresponding to the skeletons of polymer chain backbones. Such molecular structures are organized on a lattice under the excluded volume condition. An example of such representation of a linear macromolecule on the face centered cubic (fcc) lattice is shown in Figure 1.

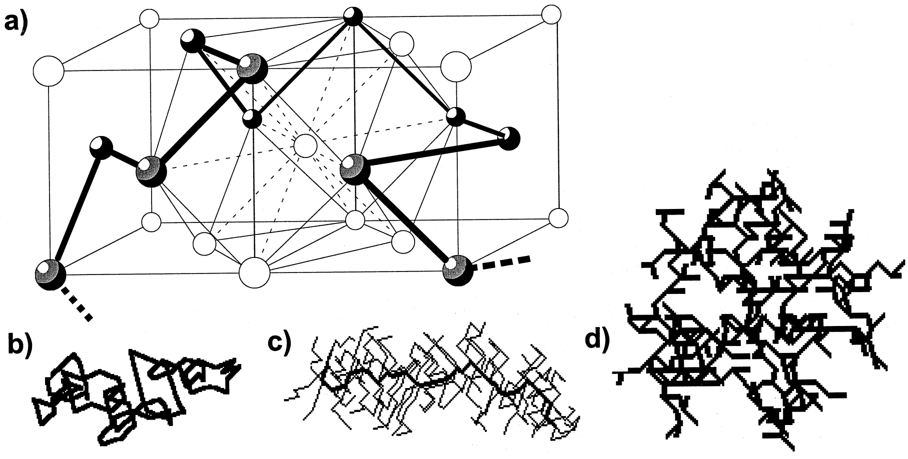


Figure 1. Illustration of representation of a linear chain (a) on the fcc lattice by means of beads connected by non breakable bonds and examples of other simulated macromolecules: (b) catenane with 8 rings, (c) brush molecule with 40 side chains grafted to the linear backbone and (d) a dendrimer of 5th generation

Some other more complex simulated structures are illustrated in a more simplified form. In order to provide lattice molecules with sufficient flexibility we apply concepts of the cooperative motions as described in several other publications [e.g. 5,10]. Parallel (DLL) or sequential (CMA) attempts of rearrangements of bead groups are considered. A single attempt in the CMA algorithm, for example, consists of several steps including: a random choice of a place of the rearrangement, a random choice of the direction of its attempted displacement and a test of constraints given by bonds with neighbors as well as by the excluded volume condition. Examples of moves resulting from successful attempts have been demonstrated elsewhere [e.g. 5]. The rearrangements can involve displacements of one or more beads. The displacements of beads change conformation of the molecule but its identity given by the specific architecture of the bond skeleton and positions of beads within the skeleton remains preserved. A large variety of rearrangements is possible and therefore, it is not possible to specify all of them. The CMA is suitable for studies of static properties of macromolecular models as well as for characterization of their dynamic behavior in a broad time range [7,15]. Simulations are usually performed for three dimensional systems on the fcc lattice. The lattice is used only as a coordination skeleton of the space. It helps to identify neighbors. Distances between lattice sites do not influence the rules of rearrangements in the athermal case, as considered here. In the cases when single molecules are considered, no spatial limits are assumed [11]. The sizes of molecules are only limited by memory limits of the computer or by time limits of the computation.

Motion of simulated molecules allows to generate a large number of states which can be averaged to get representative information about the structure of molecules in equilibrium. Monitoring displacements and orientations of the model molecules and of their elements in time one gets information about the dynamics. Time is defined as a number of attempted moves per single bead. The properties of the method important for simulation of complex macromolecular systems are:

- the method is very flexible in representing various kinds of complex macromolecules with variable degree of simplification,
- the model for the dynamics is the same for both small simple molecules and large macromolecules and does not require adjustments to particular structures,
- the simulation is very fast which allows to consider large systems in a broad time range on small computers (e.g. PC),
- the DLL version is a parallel method in which motion attempts of all elements are considered simultaneously, it should be very suitable for parallel computing but this possibility is not yet exhausted.

Single Macromolecules

As examples of characterization of properties of single macromolecules, results obtained for dendrimers, stars [12], microgels and catenanes [11] will be here briefly summarized. A characterization of structure is made by means of a number of quantities describing sizes, orientations and distributions of elements within the macromolecules. For each type of the molecular architecture a characteristic set of parameters can be defined. Examples are shown in Table 1 for some structures considered. Linear chains are used as a reference system with which the more complex systems are compared.

Table 1. Simulated structures and their parameters.

Polymers	Parameters	Range of variation	References
linear	chain length	1 - 800	11,15
cyclic	ring length	1 - 800	11
stars	number of arms	2 - 64	6,12,13,15 and this paper
	arm length	10, 20, 40, 80	
dendrimers	generation	1 - 9	this paper
	spacer length	1 - 10	
	coordination at branching points	3	
combs	cackbone length	10 - 400	5,14
	side chain length	1 - 50	
	grafting density	0.2 - 1	
catenanes	number of rings	2 - 64	11
	ring size	10 - 200	
microgels	particle size	200 - 800	15 and this paper
	number of cross-links per monomer	0 - 0.08	

Molecular sizes are usually characterized by the radii of gyration which can change in a broad range for the same molecular mass but different macromolecular architrcture. Examples of dependencies of the mean squared radius of gyration for various single macromolecules on their molecular mass are shown in Figure 2.

Details of intramolecular arrangement of elements are usually characterized by the density distribution or the bead-bead correlation function and by its analog in the reciprocal space i.e. the form factor which can correspond directly to results obtained in neutron, X-ray or light scattering experiments with such macromolecules [12]. Different intramolecular arrangements lead to different properties of single macromolecules which can also be analyzed in the simulated systems.

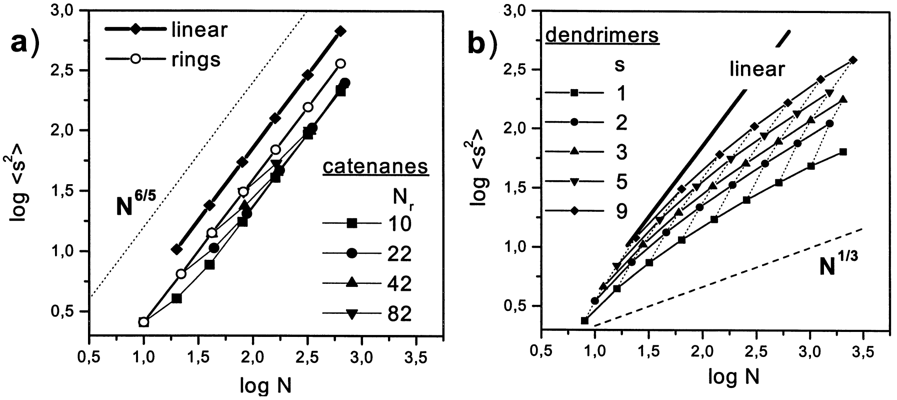
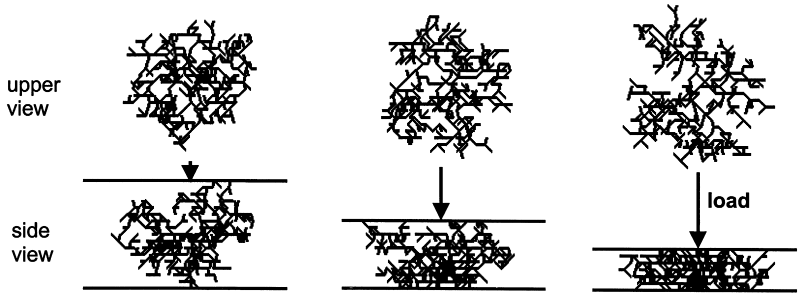


Figure 2. Mean squared radius of gyration as a function of total molecular mass for simulated polymers with various architectures: linear, rings, catenanes and dendrimers. For catenanes (a) the molecular mass is dependent on two parameters: number of rings and the ring size. For dendrimers (b) the molecular mass is given by the generation number and the length of spacer between the branching points.



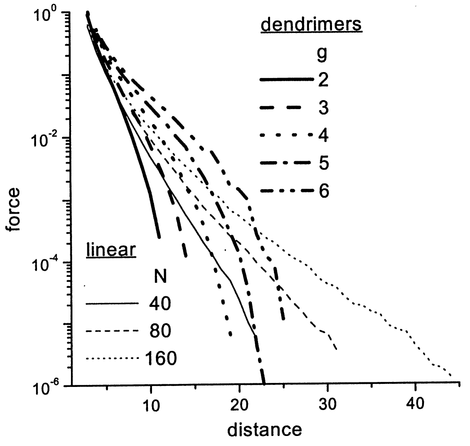


Figure 3. Illustration of the single dendrimer deformation in a computer experiment. Results in the form of force-deformation curves are shown as determined for dendrimers of various generations (g) and for linear chains of various lengths (N).

In Figure 3 an example of the force-deformation dependence is shown which has been determined for both linear chains and dendrimers under squeezing single macromolecules between two parallel walls. A remarkable difference in properties between linear chains and dendrimers is seen. The forces necessary to deform the compact structure like a dendrimer are considerably higher than these necessary to squeeze the linear chain. It is also seen that the hardness of dendrimers increases by orders of magnitude with increasing generation. The structures of dendrimers at various stages of deformation shown in the upper part of Figure 3 demonstrate a high resolution with which the analysis of intramolecular details can be performed taking also into account the different projections of the system.

Bulk Systems

The simulation methods considered here provide a unique possibility of a very effective simulation of dense systems of complex molecules i.e. systems in which all or nearly all lattice sites are occupied. Models of macromolecular melts are considered here in analogy to models of single macromolecules i.e. as systems of structureless beads connected by bonds but occupying all lattice sites in the system. It is a characteristic feature of this algorithm that types of local conformational changes are not precisely specified. All changes of polymer conformations which satisfy the assumed conditions of system continuity and non breakability of bonds are allowed. This makes the algorithm non specific for any type of polymer architecture. During motion, identities of polymers given by numbers and sequences of beads within chains are preserved. Systems which can be considered as representing melts of linear or cyclic chains, stars, combs etc. have been simulated. Various correlation functions monitored in time allow to determine relaxation times of corresponding objects (bonds or chains) and the mean squared displacements allow to determine diffusion constants. These results have shown that the dynamic behavior of simulated systems of linear chains well corresponds to behavior of real polymer melts [15]. The DLL version appeared very suitable to represent the local dynamics in dense polymer systems [9]. It has been shown, that the τ_S vs. N dependence (τ_S -segmental relaxation time) explicitly represents the effect of chain length on local dynamics. When the chain relaxation times are normalized by the segmental mobility described by τ_S they nearly satisfy the N^2 dependence as expected for the Rouse chains. On the other hand, the CMA appeared very effective in representing the dynamic properties of long linear chains in a melt [15]. The diffusion constants in the simulation reach for long chains the well known scaling dependence $D \sim N^{-2}$ and the relaxation times of chains reach the scaling low $\tau \sim N^{\omega}$, with $\omega>3$, as observed in chain length dependencies of melt viscosities for long chains. The high efficiency of the method allows now to extend the sizes of considred systems up to still suitable for chains of length N=3200.

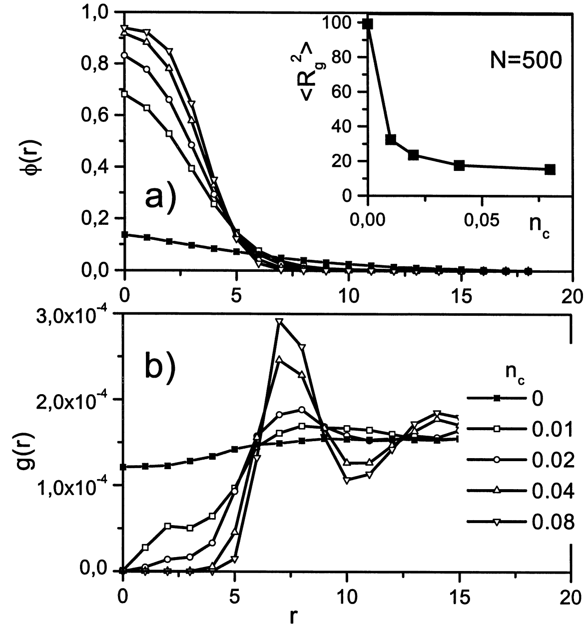


Figure 4. Static properties of simulated microgel melt: (a) the intra-particle density distributions and the sizes of particles (the insert) for various cross-linking densities and (b) the pair correlation functions of particle centers of mass for variable density of cross-links per monomer.

Complex polymeric systems such as melts of multiarm stars or melts of micelles in microphase separated block copolymers seem to show a complex dynamic behavior resulting from ordering of the macromolecules or micelles [13,16,17]. Results of simulated dense systems of this kind of macromolecules have shown that the structure develops due to strong excluded volume effect between structural elements on the macromolecular scale [6]. This leads to additional dynamic relaxation modes, which although taking place on the macromolecular size scale, seem to have many similarities with the cooperative rearrangements considered in the dynamics of small molecules in the simple liquid [9]. Here, we demonstrate an example of a melt of microgel particles which can be regarded as representative in behavior also for other compact polymer architectures such as multiarm stars, dendrimers, copolymer miceles etc. Figure 4 shows the effects of various parameters of the microgel intramolecular structure on an order in the corresponding melt. The pair correlation functions of particle centers of mass indicate the ordering increasing with increasing density of crosslinks per particle. Characteristic for such systems is the ordering in the melt consisting in an adjustement of spatial arrangement of the macromolecules to fill the space as effectively as possible under the strong excluded volume interaction on the macromolecular level. Such a structure involves considerable changes in the dynamics of the microgel mets with respect to melts consisting of linear polymers. The flow in such systems becomes controlled not by the chain orientation relaxation but by an additional slow relaxation process which is attributed to cooperative rearrangements within the ordered state. This leads to a long time living position correlation of the microgel particles which is analogous to the extra slow mode observed also for other compact chain architectures as for example for the multiarm stars [13].

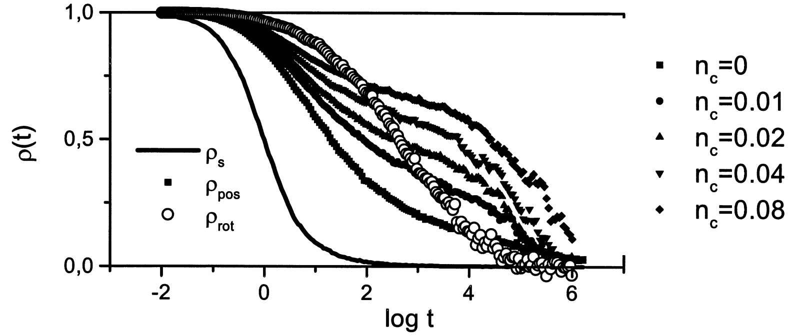


Figure 5. An example of correlation functions of bonds (ρ_b) of particle position (ρ_{pos}) and particle rotation (ρ_{rot}) for various crosslinking densities in a microgel melts.

Comparison with Experiments

Various complex macromolecules can organize themselves in a melt to structures considerably exceeding molecular dimensions due to their specific spatial forms [15,16] or specifically distributed co-units or functional groups [18,19]. Such structures can considerably influence the dynamics of systems and consequently the macroscopic properties [7,18]. The following systems have been investigated experimentally: melts of compact highly branched macromolecules [e.g. 13,16] copolymers with various distributions of comonomers [18], copolymer micelles or colloidal particles in polymer matrices [e.g. 16] and microgels [20]. The investigations involve experimental characterization of the structure using scattering and microscopy techniques, as well as a characterization of the dynamics using various relaxation spectroscopy methods. An example of the behavior of multiarm stars in the melt is illustrated in Figure 6 where the mechanical results indicate various relaxation processes from which the slowest is related to rearangements within the supramolecular order documented by means of the small angle X-ray scattering result presented in the insert. A very good agreement between the experimental observations and simulated results has been demonstarted in detail in other publications [e.g. 13].

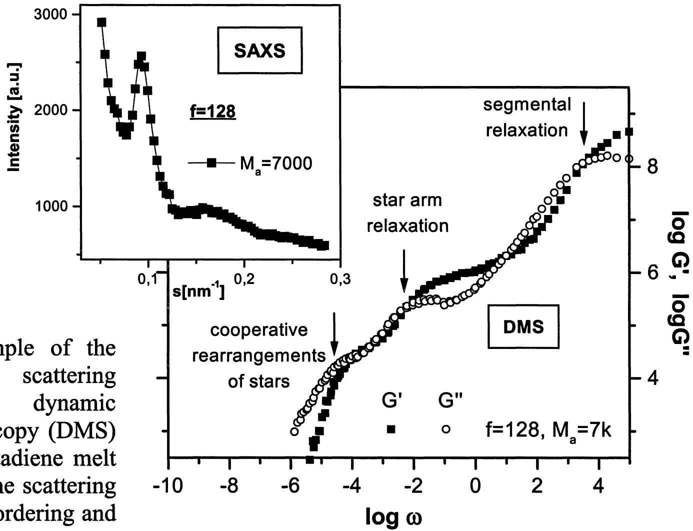


Figure 6. An example of the small angle X-ray scattering (SAXS) and dynamic mechanical spectroscopy (DMS) results for a polybutadiene melt of multiarm stars. The scattering peak indicating star ordering and various modes in the mechanical relaxation can be seen.

Conclusions

The simulation results have been analyzed with respect to various parameters defining particular architectures. Both the structure and dynamics are compared with the behavior of corresponding real systems. It is pointed out, that some of these materials represent model soft objects which order on a macromolecular scale because of strong steric interactions. This is a consequence of their complex topology, which leads to specific intramolecular monomer density distributions. It is shown, that signatures of the structures formed appear in the dynamics of these systems as extra slow relaxation processes which can control the terminal rheological behavior.

Acknowledgements

For partial support by KBN project 3T09A 043 14 (Poland). The author is grateful to all coauthors in the referenced papers for their contributions to this work.

References

1. Ambilino, D.B.; Stoddart, J.F. *Chem. Rev.* **95**,2725(1995)
2. Webster, O.W. *Macromol. Symp.* **98**,1361(1995)
3. Fetters, L.J.; Kiss, A.D.; Pearson, D.S.; Quack, G.F.; Vitus, F.J. *Macromolecules* **26**,647(1993).
4. Roovers, J.; Zbou Lin-Lin; Toporowski, P.M.; van der Zwan, M.; Iatron, H.; Hadjichristidis, N. *Macromolecules* **25**,4324(1993)
5. Gauger, A.; Pakula, T. *Macromolecules* **28**,190(1995)
6. Pakula, T.; *Comput. Theor. Polym. Sci.* **8**,21(1998)
7. Pakula, T.; Karatasos, K.; Anastasiadis, S.H.; Fytas, G. *Macromolecules* 30,8463(1997)
8. Pakula, T. *J. Comp.-Aided Mater. Design.* **3**,351(1996)
9. Pakula, T.; Teichmann, J. *Mat. Res. Soc. Symp. Proc.* **45**,211(1997)
10. Pakula, T. *J. Mol. Liquids* **86**,109(2000)
11. Pakula, T.; Jeszka, K. *Macromolecules* **32**,6821(1999)
12. Friedrich, K.; Jeszka, K.; Pakula, T. *J.Mol. Liquis* **86**,193(2000)
13. Pakula, T.; Vlassopoulos, D.; Fytas, G.; Roovers, J. *Macromolecules* **31**,8931(1998)
14. Pakula, T.; Harre, K. *Comput. Theor. Polym. Sci.* **10**,197 (2000)
15. Pakula, T.; Geyler, S.; Edling, T.; Boese, D. *Rheologica Acta* **35**,631(1996)
16. Gohr, K.; Pakula, T.; Tsutsumi, K.; Schärtl, W. *Macromolecules* **32**,7156(1999)
17. Pakula, T. *Recent Res. Devel. in Polymer Sci.* **1**,101(1996)
18. Pakula, T.; Matyjaszewski, K. *Makromol. Theory Simul.* **5**,987(1996)
19. Vlassopoulos, D.; Pakula, T.; Fytas, G.; Pitsikalis, M.; Hadjichristidis, N. *J. Chem. Phys.* **111**,1760(1999)
20. Antonietti, M.; Pakula, T.; Bremser, W. *Macromolecules* **28**,4227(1995)