Computer Simulations of Stretching and Collapse of Polymer Molecules in Solution

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Summary: Computer simulations are reported for system of linear polymer molecules, diblock copolymer and dendrimer in dilute solution without and with elongational flow. The effect of fluctuating hydrodynamics interactions (HI) on the coil-stretch transition of linear polymers and dendrimers in elongational flow is studied. The process of coiling of homo- and blockcopolymer from completely extended state is also simulated.

Keywords: block copolymers; dendrimers; elongational flow; linear polymers; rheology, simulations

Introduction

The rheological behavior of polymer solutions , both transient and steady state , is a longstanding problem of polymer science. Non-Newtonian properties of these solutions are connected with deformation and orientation of macromolecules under different flow fields . The maximum stretching of polymer chain occurs under the uniaxial elongational flow.[1] The analytical theory of polymer dynamics in an elongational flow can be developed only for simplified models such as dumbbell or Rouse models. Theory predicts the onset of the coil-stretched state transition of the chain molecule when the velocity gradient exceeds some critical value.[2] For more realistic models computer simulations are necessary. There is a lot of works devoted to the simulation of polymer chains in an elongational flow (see ref. in.[1]) The majority of works use very coarse-grained model of polymer chain: FENE dumbbell which represents whole molecule or chain consisting of FENE dumbbells representing chain segments.[3,4] There are also many papers on simulation of bead-rod models (see for example,[5-6]) but most of them do not take into account

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hydrodynamic interactions. There are also a few works on bead-rod models of chains with HI but without excluded volume (EV).[6]

In the present work we demonstrate some results of simulation of more complex models: bead-rod models of linear chain and dendrimers in elonagtional flow which take into account both EV and HI or collapse from extended state the linear bead-spring models which take into account detailed chemical structure of polymer chains.

1. Linear Polymer Chain in an Elongational Flow

We consider two linear chain models with rigid bonds. Both of them take into account excluded volume and hydrodynamic interactions. Parameters of the Lennard-Jones potential responsible for excluded volume interactions correspond to the chain in the θ-solvent In the first model (A) the neighboring rods are freely jointed into linear chain and in the second one (B) the bond angle and torsion angle potentials are added. The first model and method of simulation is described in the paper of authors.[7] The description of the second model can be found in[8] where it was used for the simulation of linear polymer chain in dilute solution under shear flow. For both models chain length was varied from N=10 to N=94.

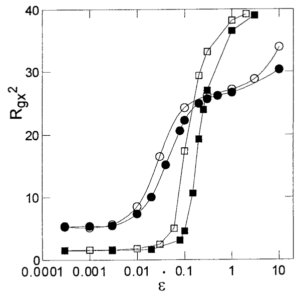

Fig.1 Dependence of mean square of the radius of gyration of chain (N=22) on flow rate. Squares – model A, circles – model B. Open symbols – without HI, filled ones – with HI

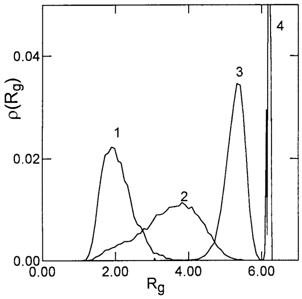

Fig.2 Distribution function of the radius of gyration at the different flow rates for model A with HI. (1) – 0.0003, (2) – 0.15, (3) – 0.3, (4) – 2.0

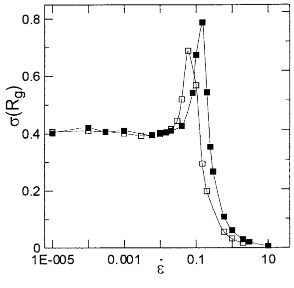

Fig.3 The dependence of the fluctuation of the radius of gyration on the flow rate. Open symbols – without HI, filled ones – with HI. Model A

The critical behavior of polymer chain in the flow appears as a step-like increase of its size in the narrow range of velocity gradients (Fig. 1). It is easy to see that deformation of less flexible model B (Fig.1) starts earlier and continues at higher elongation rates than for model A. For model A there are single critical transition rate while for model B the dependence looks like a sequence of two step-like transitions. First of them corresponds to uncoiling of chain and second – to stretching the "valence" angles. This results disagree with conclusions of[9] where chain model with bond angle and torsion angle potentials but with flexible bonds (given by FENE dumbbells) was simulated in an elongational flow. For this model the effect of the torsion potential on the dependence was negligible. The transition curve was very close to that for a freely-jointed chain. Therefore the taking into account the bond rigidity has a significant effect on the behavior of polymer chain with hindered internal rotation in the flow field. Hydrodynamic interaction shifts the transition region to higher values of flow rates for both models. One of the characteristic features of phase transition is the increase of fluctuations in the transition region. Fig.2 demonstrates the broadening of the distribution function of the gyration radius due to increase for fluctuations of mean squared gyration radius of linear chain at flow rate close to the point of transition (curve 2). Fig.3. directly shows the increase of fluctuations of the radius of gyration in the transition region for bead-rod chain A both without and with HI. The values of critical transition rate were defined by two ways: as middle point of steplike dependencies of end-to-end distance and mean square of orientation of monomers on elongational rate. The dependencies of critical transition rate (line 1 and 2) on chain length N are presented on Fig.4 for model A. For chains without and with HI this dependence can be fitted to $N^{-1.96}$ and $N^{-1.55}$ correspondingly in agrement with theoretical predictions (obtained from reciprocal longest relaxation times $1/\tau_{max}$) for Rouse ($N^{-2.0}$) and Zimm ($N^{-1.5}$) models correspondingly.

We also calculated for model A (with and without HI) values of two global relaxation times: τ_{R_g} for correlation function of the gyration radius R_g and τ_1 for the first normal mode for different chain lengths N in the absence of flow. Dependences of these times close to $N^{2.0}$ for chain without HI (Fig.4) and $N^{1.5}$ for chain with HI (not shown) were obtained. Values of the critical transition rate are close to those of reciprocal relaxation times $1/\tau_{R_g}$ (Fig.4). ,i.e. $\dot{\varepsilon}_{cr}\tau_{R_g} \approx 1$. In the model B the stretching of the chain in the flow is accompanied by the change of its equilibrium (fractions of trans and gaushe isomers (Fig.5)) and dynamic (rates of trans-gaushe transitions (Fig.6)) conformational characteristics. It is easy to see that fractions of trans and gaushe conformers as well as the rate of trans-gaushe transitions (Fig.6) change at the same interval of $\dot{\varepsilon}$ as the chain size does (Fig.1). Hydrodynamic interactions shift the transition region for both these characteristics to higher elongational rates.

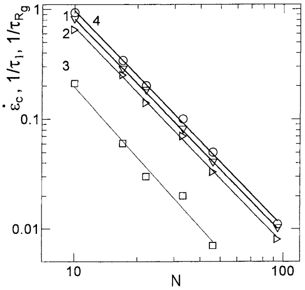

Fig.4 The dependence of critical flow rates (1,2) and reciprocal relaxation times τ_1(3) and τ_{R_g}(4) on chain length N. Model A

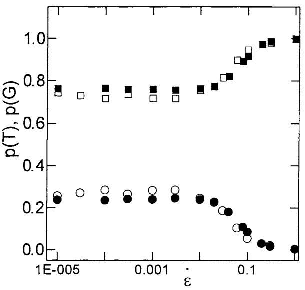

Fig.5 The dependences of the fractions of trans and gaushe conformations on the flow rate. Open symbols – without HI, filled ones – with HI. Model B

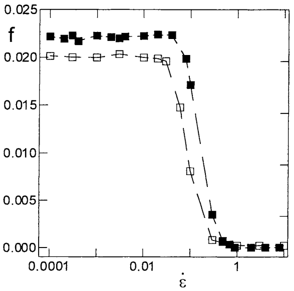

Fig.6 The dependence of the conformational transition rate on the flow rate. Open symbols – without HI, filled ones – with HI.
Model B

2. Collapse of Diblock Copolymer

Unsaturated polyesters are commonly used as matrix resins in composite applications,(ship building, car manufacture, construction etc). In these applications reinforcing glass fibers are embedded in an unsaturated polyester matrix prior to curing, in order to give the needed mechanical strength. The modification of unsaturated polyesters by poly(ethylene glycol) end groups has recently been described by Schulze et al..[10] The modification was done in order to increase the toughness of the cured unsaturated polyester (UPE), and to lower the shrinkage during curing. This is normally done by physical methods,[11] by addition of elastomer particles (low profile additives) to the matrix. Chemical modification can also be used,[12] for example through the incorporation of long chain diols or unsaturated acids into a polyester chain. In the recent work of Schulze et al..[10] the modification was done by use of the end-group reaction of a carboxyl-terminated unsaturated polyester with poly(ethylene glycol) (PEG) mono methyl ethers of various molecular weights (range 350 to 2000 g/mol). Analysis revealed that diblock copolymers of the AB type (see Fig. 7a) were formed, and that the diblock copolymers contained usually one poly(ethylene glycol) end group per polyester segment.

Properties of block copolymers in the bulk were intensively studied in computer simulations by use of different coarse grained models by Monte Carlo (MC)[13] and molecular dynamics (MD) [14] methods. Of course for more precise description of block copolymers the MD simulation with full atomic details should be used but this approach requires enormous computer time. Nevertheless some conclusions about their structure and phase behavior can be obtained from consideration of only one or two macromolecules. For example Choi et al..[15] studied the miscibility and structure of polyethylene and polypropylene (PP) mixtures by simulation of collapse of two initially extended PE and PP molecules placed near each other. In the present work we apply a similar approach to the study of the collapse and final structure of an initially

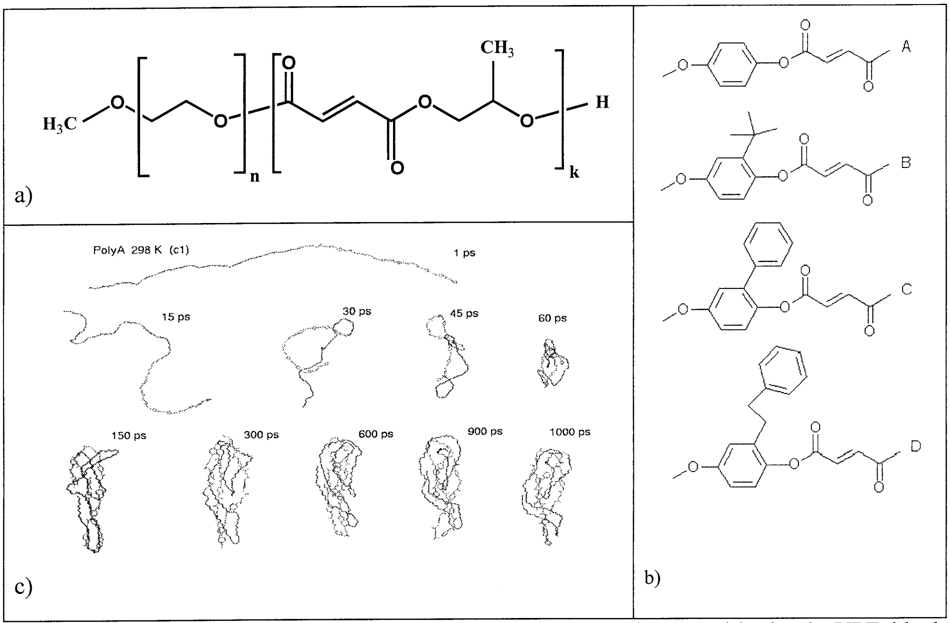

Fig.7 a) Chemical structure of diblock copolymer of PEO and UPE with simple UPE block. b) Chemical structure of different second (UPE) block, c) Selected snapshots of diblock copolymer during relaxation extended molecule of AB diblock copolymer of polyethylene glycole (PEG) and unsaturated polyesthers (UPE) by MD. Such an extended state can be obtained for example in a strong elongational flow (see Fig.1). Different chemical structures of UPE block (B) (see Fig. 7a and 7b). Both PEG and UPE blocks had nearly the same molecular weight - 2000 g/mol. For comparison the collapse and the final structures of UPE and PEG homopolymers of the same total molecular weight (4000 g/mol) were simulated. The initial conformations were prepared and MD simulations were performed by using the molecular modelling software package Insight II and Discover from MSI.[16] The force fields CVFF and COMPASS were used. The simulations were performed in a vacuum at constant temperature 298K by the use of the velocity scaling or Andersen algorithms. In the last case the collisions with virtual solvent particles reproduce partially the effect of a solvent. The use of the above mentioned force fields for atom-atom interactions without explicit account of the solvent means that both blocks were simulated in a poor solvent .

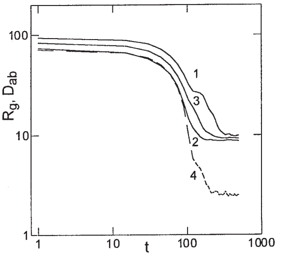

Fig.8 Time dependence of radius of gyration of PEO (1), UPE (2), diblock copolymer (3) and distance between centers of mass of blocks in diblock copolymer during collapse.

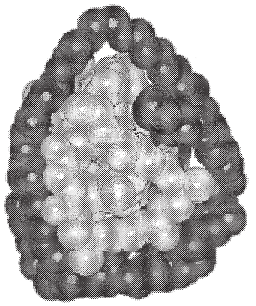

Fig.9 Snapshots of final conformation of diblock copolymer after 1000ps relaxation.

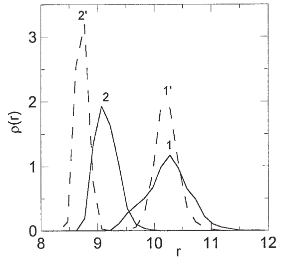

Fig.10 Distribution function of the radius of gyration of PEO (1) and UPE (2) blocks in homopolymers (1,2) and in diblock copolymer (1',2')

Changes of the conformation of copolymer chain in the process of the collapse are shown in Fig. 7c.and Fig.8 .One can distinguish two stages of this process. On the first stage(during the first 30-40ps) both blocks remain to be stretched. The intra- and interblock interactions are weak and conformations of blocks don't change significantly. On the second stage (during 40-200 ps) the blocks decrease their size and start to interact with each other .The increase of the strength of interactions accelerates the process of collapse and vice versa. As a result the structure arises where the UPE block forms the core of the polymer particle, and the more flexible PEO forms the shell.(Fig.9) The centres of mass of two blocks are very close to each other (Fig.8, curve 4). This structure does not change essentially during the simulation time (~1000 ps) at least.

We have thus a partial separation of the two blocks where one block is placed inside the another one. Such a structure is not common . For example in[15] the collapse of two (PE and PP) entangled molecules led to the segregation of blocks in two separate (dumb-bell like) domains which are not interpenetrate.

It is interesting to compare the sizes (R_g) of UPE and PEG block in the final collapsed state of diblock copolymer AB with those of these blocks placed into their own homopolymer (in this case homopolymer consists of two equal blocks AA or BB. Fig. 10 shows the distribution function of the radius of gyration R_g for blocks A and B both in the homopolymers and copolymer . The UPE block (B) included into copolymer AB is essentially more compact than that in the BB homopolymer. At the same time the size of the PEG block (A) in the copolymer occurs to be larger than in homopolymer. Such a behavior is a consequence of a core-shell structure of the UPE-PEG diblock copolymer.

3. Dendrimer under an Elongational Flow

As for a linear macromolecule we have used the method of Brownian dynamics for the simulation

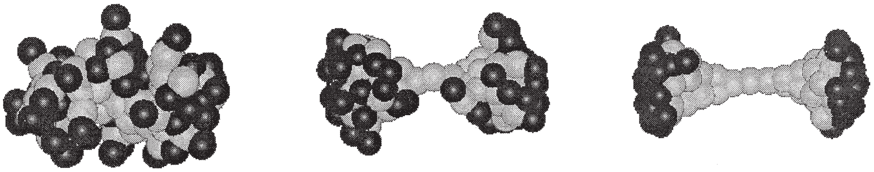

Fig.11 Snapshots of dendrimers of fifth generation with HI at different flow rates: a) 0.1, b) 1.0 and c) 6.0 . Light beads - internal monomers, dark beads – terminal ones

of a dendrimer molecule in the dilute solution under an elongational flow . The models similar to the chain model A (see part 1 of this paper) with rigid bonds, excluded volume and with and without hydrodynamic interactions were considered. The neighbouring bonds are freely jointed and there is only one bond between successive branching points. Because of the flow symmetry the core with functionality F=2 was chosen. Dendrimers from 1 to 5 generations were simulated. For all other branching points F was equal to 3. More detailed description of model can be found in[17] where it was used for the simulation of a dendrimer in dilute solution under shear flow . Fig. 11 (a,b,c) shows the conformations of a dendrimer under different elongational rates $\dot{\varepsilon}$.

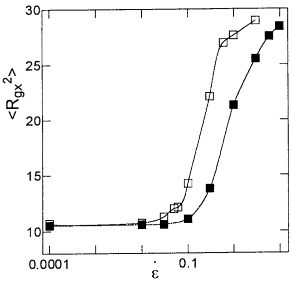

Fig.12 The dependence of mean square of the radius of gyration of dendrimer of 5th generation on the flow rate. Open symbols – without HI, filled ones – with HI

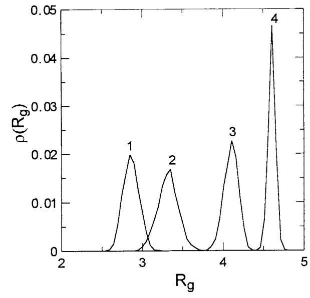

Fig.13 The distribution function of the radius of gyration of dendrimer of 5th generation with HI at different flow rates: 1- 0.0, 2 – 0.3, 3 - 1.0, 4 – 6.0

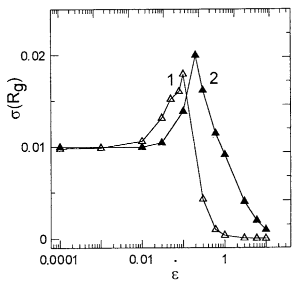

Fig.14 The dependence of the fluctuation of the radius of gyration of dendrimer of 5th generation on the flow rate. . Open symbols – without HI, filled ones – with HI

Fig.12 shows the dependence of its size on $\dot{\varepsilon}$. In the absence of the flow the dendrimer molecule has a nearly spherical shape. At small $\dot{\varepsilon}$ the shape of the dendrimer becomes to be anisotropic (Fig.11a) but its size changes only slightly (Fig.12) . The significant change of the dendrimer size occurs in the narrow region $\dot{\varepsilon}$ (Fig.12) both for models with and without HI. In the middle of the transition region the dendrimer molecule has a dumbbell-like shape (Fig.11b) where two dendrons are separated but terminal groups (shown by black on the picture) are distributed along the whole dendron. At the end of transition the dendrimer has a shape similar to two co-axial cones connected by their vertexes (Fig 11.c). Terminal groups are located on the periphery of dendrons. Such a conformation is a result of the competition between the stretching effect of the flow and repulsion between monomers which doesn't allow to align all monomers along the flow. The behavior of a dendrimer in the flow has common traits with that of a linear chain : the size of the dendrimer remains unchanged below the some velocity gradient and increases step-like in the narrow range of flow rates. Fluctuations of R_g in this region increase and their magnitude is a little larger for the impenetrable dendrimer than for a free–draining one (Fig.14). Hydrodynamic interactions shift the transition region to higher values of flow rates.

But there are several distinctions:

(a) the value of the critical gradient for a dendrimer is much larger than that for a linear chain of the same molecular mass. (b) the full alignment of all monomers along the flow is impossible, (c) similar to a linear chain some broadening of distribution function for gyration radius of the dendrimer (Fig.13) in the transition region is observed.

Acknowledgments

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