

MOLECULAR SIMULATION OF DENDRIMERS UNDER SHEAR



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Abstract

In this work flow properties of dendrimers are studied with the aid of molecular simulations. For the first time the results of the nonequilibrium molecular dynamics simulations of the dendrimers in the melt are reported. Molecules are modelled at the coarse-grained level using the bead-spring model. The objective of this research is to analyse the influence of the molecular topology on the macroscopic flow behaviour of the melts. Systems of dendrimers of generations 1 to 4 undergoing planar shear are compared to the melts composed of linear chain polymers. The internal structure and shape of dendrimers is extensively analysed. The response of the molecules to the shearing in the form of stretching and alignment is studied. The correlation between the onset of shear thinning and the onset of deformation of molecules is observed. The changes in the fractal dimensionality of dendrimers due to shearing are also analysed. Dendrimers, due to their highly branched structure and compact globular conformations in the melt, are found to behave differently when sheared, compared to traditional linear polymers. Unlike linear polymers, they do not undergo transition from the Rouse to the reptation regimes. This effect is explained in terms of the suppressed entanglement between molecules. Moreover, dendrimers when compared to linear chain systems exhibit lower Newtonian viscosity, onset of the shear thinning at higher strain rates, and less pronounced shear thinning in the non-Newtonian regime. They can be used as rheology modifiers, as it is shown in the preliminary results obtained from the simulations of the dendrimer-linear polymer blends. In agreement with other theoretical and experimental studies, dendrimers in the melt are found to have compact space-filling structure with terminal groups distributed throughout the interior of the molecule. Suggestions for the further study of dendrimers via molecular simulations are made.

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Declaration

I hereby declare that the thesis entitled “Molecular Simulation of Dendrimers under Shear”, and submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy in the School of Information Technology of Swinburne University of Technology, is my own work and that it contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the thesis. To the best of my knowledge and belief, it contains no material previously published or written by another person except where due reference is made in the text of the thesis.

Jarosław T. Boško

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Publications from this thesis

The following papers have been based on part of this work:

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Notation

Abbreviations

aRDF	atomic radial distribution function
EDA	ethylenediamine
FENE	Finitely Extensible Nonlinear Elastic potential
LJ	Lennard-Jones potential
MC	Monte Carlo
MD	Molecular Dynamics
mRDF	molecular radial distribution function
NEMD	Non-Equilibrium Molecular Dynamics
NMR	nuclear magnetic resonance
PAMAM	poliamidoamine dendrimer
PPI	poly(propyleneimine) dendrimer
RDF	radial distribution function: atomic;
SAXS	Small Angle X-Ray Spectroscopy
SCF	Self-Consistent Field method
WCA	Weeks-Chandler-Anderson potential

Latin alphabet

b	<i>spacer</i> – number of beads in a linear unit of a dendrimer
b	asphericity
c	acylindricity
d_f	fractal dimensionality
$D_b G_g$	dendrimer of generation g with spacers of the length b
f	functionality of the branch groups of a dendrimer
f_c	functionality of the core of a dendrimer
\mathbf{F}_i	force acting on molecule i
$\mathbf{F}_{i\alpha}$	force acting on bead α in molecule i
g	generation number
$g_A(r)$	atomic radial distribution function

$g_M(r)$	molecular radial distribution function
\mathbf{I}	tensor of inertia, unit tensor
k	spring constant of the FENE potential
k_B	Boltzmann constant
l_{bond}	bond length
L_1, L_2, L_3	mean eigenvalues of the tensor of gyration
L'_1, L'_2, L'_3	eigenvalues of the mean tensor of gyration
m	mass of a single bead
M	mass of a molecule
N	number of molecules
N_α	number of beads composing a single molecule
N_{end}	number of terminal groups in a dendrimer
N_{total}	total number of beads composing the system
N_1	first normal stress difference
N_2	second normal stress difference
p	pressure
\mathbf{P}	pressure tensor
\mathbf{P}^A	atomic pressure tensor
\mathbf{P}^M	molecular pressure tensor
P_{xy}	xy element of the pressure tensor
\mathbf{p}_i	total momentum of molecule i
$\mathbf{p}_{i\alpha}$	momentum of bead α in molecule i
Q	damping factor in the NpT algorithm
\mathbf{r}_i	position of the centre of mass molecule i
$\mathbf{r}_{i\alpha}$	position of bead α in molecule i
r_{ij}	distance between centres of mass of molecule i and molecule j
R_0	finite extensibility of the FENE spring
\mathbf{R}_g^2	tensor of gyration
R_g	radius of gyration

S	order tensor
Δt	integration time step
T^A	atomic temperature
T^M	molecular temperature
U	interaction potential energy
U_{ij}^{FENE}	FENE interaction energy between beads i and j
U_{ij}^{WCA}	WCA interaction energy between beads i and j
V	volume of the simulation box

Greek alphabet

$\dot{\gamma}$	shear rate
$\dot{\gamma}_0$	shear rate of the onset of shear thinning
ε	LJ energy parameter
$\dot{\varepsilon}_{xx}$	compression rate along x axis
η	shear viscosity in the steady shear
η_0	zero shear viscosity
η^*	complex viscosity in the oscillatory shear
$[\eta]$	intrinsic viscosity
κ^2	relative shape anisotropy
ρ	bead concentration/density
σ	stress tensor
σ	LJ length parameter
ζ	thermostatting coefficient
τ_0	maximum relaxation time
χ	birefringence extinction angle
Ψ_1	first normal stress coefficient
Ψ_2	second normal stress coefficient
ω	frequency in the oscillatory shear
ω	molecular angular velocity