Molecular Structure of Azobenzene-Containing Systems from Classical MD Simulations

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Motivation

Photoreaction units: azobenzene, or azo-containing 1,3,5-benzene-tricarboxamide

Experimental observations [1,2]

What happens at the macroscopic scale?
Symmetry and volumetric differences

Inscription of SRG on azo-polymers [3]:

Benefit from reversibility conversion between two isomers under external stimuli

Photoreactive thin films containing azo-groups (i) azobenzene or (ii) three-armed star-shaped photoreaction unit with 1,3,5-benzene-tricarboxamide core) react strongly to light irradiation

Polymer topography deforms according to polarization and intensity distribution in the light interference pattern

It results in surface relief grating (SRG) formation.

Details of microscopic approach

Basic driving mechanism
I. Photoisomerization of azo-group

trans-

V(θ)=D(θ)cosθ, V0=10−19 J m−2

θ: strength of the potential; V0: intensity of the light

II. Two ways of coupling of azobenzene-containing unit to a polymer chain (4,5)

Physical attachment: ionic interactions

Chemical attachment: covalent bond

III. Local alignment of azobenzenes to electric field vector (orientation approach [6])

Coarse-grained model: United CH, atoms & Gay-Berne rods (azobenzenes)

Orientation of azo-molecule:

Wθ(θ, β) - distribution function

Effective potential:

U(θ) = NωθV0cos2β

Two questions: (i) relation of microscopic details to the macroscopic response and (ii) prediction of the sign and magnitude of light-induced stress tensor (for the microscopic theory [6], Wθ(θ, β) - distribution function defined by both the potentials of internal rotations and the length of spacer).

Conclusions & Outlook

A present study combines coarse-grained and full-atomistic MD simulations of (i) amorphous polymer with azobenzene moiety as side chain and (ii) system composed of three-armed star-shaped units and represents preliminary steps towards a comprehensive multiscale model for azobenzene-containing systems.

Using coarse-grained MD simulations, the deformation of the illuminated volume element is obtained on molecular level.

The distributions of polar and azimuthal angles for chromophores orientations are received at different temperatures and light intensities and their analysis is performed in terms of nematic order parameters calculated with respect to the backbone.

It is shown that the reason for the light-induced deformation of azo-containing polymer below the glass transition temperature is the reorientation of azo-units with unique propeller-like conformation.

The self-assembly of trans-ctomers of three-armed star-shaped photoreaction units from an arbitrary dispersed initial configuration to a columnar structure is observed using all-atom MD (H-bonds/CH-stabilization).

The “switching” of the isomerization state from trans-to-cis alters the degree of interlayer stacking and leads to twisted arrangements of individual components and volumetric changes of the packing motif.

References

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Coarse-grained MD modelling

Field component of backbones gyration tensor

Sample size along the field

MD simulations of amorphous polymer azo-polymer [7]

Main effects:
- (2) propeller-like conformations
- (i) reorientation of propeller’s main axis & backbones mass redistribution → elongation of an illuminated sample

A closer look: Atomic details

Three-armed star-shaped photoreaction unit with 1,3,5-tricarboxamide core

SNG-experiments [8]

Self-organization of similar azo-systems in solvents (immiscibility & crystal packing [10,11])

Molecular structure of trans- & cis-isomers: symmetry and volumetric differences

Predicting crystalline structures: packing diagrams

Selection criteria:
- Alignment of mesogenic groups (trans-isomer)
- n-stacking (central benzene ring)
- Intramolecular H-bonding
- Density

Interlayer distance of chromophores, the azobenzene core fits the best part of the system. Asymmetry of the molecules demonstrates the packing intensity (% of unit cells with packing)

Interlayer packing density of azobenzene monolayers

Thickness of azobenzene monolayers