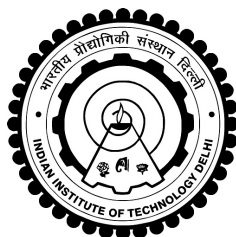


**STUDIES OF DISPERSION AND SELF-ASSEMBLY
OF GRAFTED NANOPARTICLES IN POLYMERIC
SYSTEMS**

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MAY 2020

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by

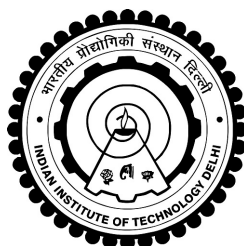
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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology Delhi

May 2020

Dedicated to the Almighty...

Certificate

This is to certify that the thesis titled “**Studies of Dispersion and Self-assembly of Grafted Nanoparticles in Polymeric Systems**” being submitted by **Ms. Supriya Gupta** in the Department of Chemical Engineering, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of bona-fide research work carried out by him under my guidance and supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree. The results contained in this thesis have not been submitted for the award of any other degree, associateship or similar title of any university or institution.

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Ultimately, I dedicate this thesis to the Almighty for being with me through every path of my life.

New Delhi

Supriya Gupta

Abstract

The incorporation of small amount of nanoparticles in polymers results into phenomenal improvement in material properties when at least one dimension of the particles is smaller than the size of polymeric chains. The nano-scale of particles ensures that large fraction of polymer segments is in contact with the particles to bring out the synergistic interaction between the constituents leading to dramatic enhancement in material properties. The dispersion of nanoparticles in polymer matrix is achieved by inducing steric repulsion realized by grafting polymeric chains on particles. The first part of the present study addresses the dispersion of clay nano-sheets grafted with polymeric chains in a matrix of varying architecture. With the help of self-consistent field theory, we construct the distance dependent inter-particle interaction potential between a pair of nano-sheets grafted with polymeric chains dissimilar to the matrix polymer with respect to either chain size, chain architecture or chemical structure. Upon replacing linear polymeric chains of the matrix polymer with multi-armed star polymer of same degree of polymerization, the strength of attraction is found to be weakened and is completely eliminated for high degree of branching. The compactness of star molecule overcomes the entropy driven depletion between nano-sheets leading to wetting of brush with purely repulsive potential, an indicative of exfoliated dispersion. Thus, the clay sheets can be better dispersed in a star polymer compared to linear polymer matrix.

Beyond dispersion, the controlled self-assembly of nanoparticles in a polymer matrix offers a great potential to produce highly ordered nanostructures with far superior opto-electronic properties. The templated ordering of nanoparticles is increasingly gaining attention to produce advanced nano-materials with wide ranging technological applications. Block copolymers, by virtue of their fascinating ability to self-organize to yield plethora of interesting ordered phases, provide ideal templates to achieve particle ordering. Using self-consistent field theory, we examine the self-assembly of polymer grafted spherical nanoparticles in lamellar mesophase of symmetric ABA triblock copolymer. The localization behaviour of B-grafted nanoparticles is found to be qualitatively different from that of the A-grafted particles. In particular, the absence of free ends and the bridge conformation of mid-block tend to reduce the spatial

segregation of B-grafted particles at the center of B-domain and promote segregation of particles at the domain interface, a behavior in contrast to AB diblock copolymer. The spatial localization of particles, governed by the interplay of enthalpic and entropic contributions to the free energy, is found to be strongly influenced by particle size, selectivity, volume fraction, and number & size of grafted chains.

Physical confinement of block copolymers plays an important role in generating a rich variety of novel ordered phases not seen in bulk systems. These novel ordered microstructures, arising mainly out of structural frustration and confinement-induced entropy loss, are ideal templates to self-assemble nanoparticles. For a mixture of diblock copolymer and grafted nanoparticles, the morphology under cylindrical pore confinement and ensuing particle ordering are studied in both two and three dimensions. Various equilibrium morphologies are observed depending upon the degree of confinement, particle loading, density of grafted segments and selectivity of particle core to the polymeric species. The curvature of the circular pore strongly influences the localization behaviour of particles. Further, the physical confinement produces, apart from concentric lamellar and cylindrical phases, some interesting 3-d structures like helical ordering. Incorporation of spherical nanoparticles grafted with polymer chains chemically identical to the helical block leads to helical ordering of nanoparticles. Such chiral structural motifs generated from achiral polymeric molecules are fascinating due to superior performance in sophisticated optical functions. The roles of confinement size, particle load and grafting density in self-assembly behavior of nanoparticles and ensuing microstructure are examined.

In order to generate novel multicomponent helical structures, block copolymers with topologically complex architectures, like three-armed ABC star polymer and four-armed ABCD star polymer are also investigated for their equilibrium states under cylindrical nanopore confinement. ABCD star tetrablock copolymer exhibits rich self-assembly behavior with myriads of three-dimensional ordered phases ranging from one, two and three components helices to honeycomb structures depending upon the block fractions and the size of cylindrical nanopore. The comprehensive understanding of the self-assembly behavior enables one to design novel nanostructured materials with desired material properties.

सारांश

पॉलिमर में छोटी संख्या में नैनोकणों के शामिल होने से भौतिक गुणों में अभूतपूर्व सुधार होता है जब कणों का कम से कम एक आयाम पॉलिमरिक श्रृंखलाओं के आकार से छोटा होता है। कणों का नैनो-स्केल यह सुनिश्चित करता है कि बहुलक खंडों का बड़ा हिस्सा द्रव्य गुणों में नाटकीय वृद्धि के लिए घटकों के बीच सहक्रियाशीलता को बाहर लाने के लिए कणों के संपर्क में है। बहुलक मैट्रिक्स में नैनोकणों का फैलाव स्टेरिक प्रतिकर्षण को उत्प्रेरित करके किया जाता है जो कि कणों पर पॉलीमरिक श्रृंखलाओं को ग्राफ्ट करके प्राप्त किया जा सकता है। वर्तमान अध्ययन का पहला हिस्सा अलग-अलग स्थापत्य के मैट्रिक्स की पॉलिमर श्रृंखलाओं के साथ ग्राफ्टेड क्ले के नैनोशीट के फैलाव को संबोधित करता है। स्व-सुसंगत क्षेत्र सिद्धांत की सहायता से हम बहुलक श्रृंखला से ग्राफ्टेड नैनोशीट की एक जोड़ी के आपस में दूरी-निर्भर अंतर-कण संपर्क क्षमता का निर्माण करते हैं जो कि मैट्रिक्स बहुलक से श्रृंखला आकार, श्रृंखला वास्तुकला या रासायनिक संरचना में भिन्न होता है। मैट्रिक्स बहुलक के रैखिक बहुलक श्रृंखलाओं को एक ही डिग्री के बहुलकीकरण के बहु-सशस्त्र स्टार बहुलक के साथ बदलने पर, आकर्षण की शक्ति कमजोर पाई जाती है और उच्च स्तर की शाखाकरण के लिए पूरी तरह से समाप्त हो जाती है। स्टार अणु की संरचना नैनो-शीट के बीच एन्ट्रापी-चालित कमी को पार कर जाती है, जो शुद्ध रूप से प्रतिकारक क्षमता के साथ ब्रश को गीला करने की ओर ले जाती है, जो एक्सफ़ोलीएटेड फैलाव का संकेत है। इस प्रकार क्ले की चादरें रैखिक बहुलक मैट्रिक्स की तुलना में एक स्टार बहुलक में बेहतर ढंग से छितरी जा सकती हैं।

फैलाव से परे, एक बहुलक मैट्रिक्स में नैनोकणों के नियंत्रित स्व-असेंबली, सुपीरियर ऑप्टोइलेक्ट्रॉनिक गुणों के साथ उच्च क्रमित नैनोस्ट्रक्चर का उत्पादन करने की एक बड़ी क्षमता प्रदान करता है। नैनोकणों का क्रमबद्ध क्रम व्यापक रूप से तकनीकी अनुप्रयोगों के साथ उन्नत नैनो-सामग्रियों का उत्पादन आजकल काफी चर्चे में है। ब्लॉक कोपोलिमर, क्रमित चरणों के ढेरों को प्राप्त करने की अपनी आकर्षक क्षमता के आधार पर, कण क्रम प्राप्त करने के लिए आदर्श टेम्पलेट प्रदान करते हैं। स्व-सुसंगत क्षेत्र सिद्धांत का उपयोग करते हुए, हम सममितीय एबीए ट्राइब्लॉक कॉपोलीमर के लैमेलर मेसोपेज में बहुलक ग्राफ्टेड गोलाकार नैनोपार्टिकल्स की स्व-समूहन की जांच करते हैं। बी-ग्राफ्टेड नैनोकणों का स्थानीयकरण व्यवहार ए-ग्राफ्टेड कणों से गुणात्मक रूप से भिन्न पाया जाता है। विशेष रूप से, मुक्त सिरों की अनुपस्थिति और मध्य-ब्लॉक के पुल की विरूपण बी-डोमेन के केंद्र में बी-ग्राफ्टेड कणों के स्थानिक अलगाव को कम करते हैं और डोमेन इंटरफ़ेस पर कणों के अलगाव को बढ़ावा

देते हैं, जो कि एबी डार्ब्लॉक कॉपोलीमर के विपरीत व्यवहार है। कणों की स्थानिक स्थानीयकरण, मुक्त ऊर्जा में एन्थैल्पिक और एन्ट्रॉपिक योगदान के परस्पर क्रिया द्वारा नियंत्रित, कण आकार, चयनात्मकता, आयतन अंश, और ग्राफ्टेड श्रृंखलाओं के संख्या और आकार से दृढ़ता से प्रभावित पाया जाता है।

ब्लॉक कोपोलिमर्स का भौतिक परिरोध थोक व्यवस्था में नहीं देखे जाने वाले नव क्रमबद्ध चरणों की एक समृद्ध विविधता पैदा करने में महत्वपूर्ण भूमिका निभाता है। मुख्य रूप से संरचनात्मक हताशा और परिरोध-प्रेरित एन्ट्रापी नुकसान से उत्पन्न होने वाले ये नव आदेशित माइक्रोस्ट्रक्चर, स्व-एकत्र नैनोकणों के लिए आदर्श टेम्पलेट हैं। डार्ब्लॉक कोपोलीमर और ग्राफ्टेड नैनोकणों के मिश्रण के लिए, बेलनाकार रोम परिरोध और आगामी कण आदेश के तहत आकृति विज्ञान का अध्ययन दो और तीन आयामों में किया जाता है। विभिन्न सन्तुलन आकृति विज्ञान, परिक्षेपण की डिग्री, कण लोडिंग, ग्राफ्टेड सेगमेंट के घनत्व और पॉलीमरिक प्रजातियों में कण कोर की चयनात्मकता के आधार पर देखे जाते हैं। वृत्ताकार छिद्र की वक्रता कणों के स्थानीयकरण व्यवहार को दृढ़ता से प्रभावित करती है। इसके अलावा, भौतिक कारावास, गाढ़ा लामेलर और बेलनाकार चरणों के अलावा, कुछ दिलचस्प 3-डी संरचनाएं जैसे पेचदार क्रम उत्पन्न करता है। गोलाकार नैनोकणों का समावेश बहुलक श्रृंखलाओं के साथ रासायनिक रूप से पेचदार ब्लॉक के समान होता है, जो फलस्वरूप नैनोकणों के पेचदार क्रम की उत्पन्न करता है। अचिरल पोलिमरिक अणुओं से उत्पन्न ऐसे चिरल संरचनात्मक रूपांकनों को परिष्कृत ऑप्टिकल कार्यों में बेहतर प्रदर्शन के कारण आकर्षक होते हैं। नैनोकणों के स्व-समूहन व्यवहार और आगामी माइक्रोस्ट्रक्चर में परिरोध आकार, कण भार और ग्राफिटिंग घनत्व की भूमिकाओं की जांच की जाती है।

नव बहुविकल्पीय पेचदार संरचनाओं को उत्पन्न करने के लिए, सांस्थितिकी रूप से जटिल आर्किटेक्चर वाले कोपोलीमर, जैसे तीन-सशस्त्र एबीसी स्टार बहुलक और चार-सशस्त्र एबीसीडी स्टार बहुलक की भी बेलनाकार नैनोपोर परिरोध के तहत उनके संतुलन वाले अवस्थाओं की जांच की जाती है। एबीसीडी स्टार टेट्राब्लॉक कोपोलीमर ब्लॉक अंशों और बेलनाकार नैनोपोर के आकार के आधार पर एक, दो और तीन घटक हेलिक्स से लेकर मधुकोश की संरचनाओं तक के तीन-आयामी क्रमित किए गए चरणों के साथ समृद्ध स्व-समूहन व्यवहार प्रदर्शित करता है। स्व-समूहन व्यवहार की व्यापक समझ वांछित द्रव्य गुणों के साथ नव नैनोस्ट्रक्चर सामग्री को डिजाइन करने में सक्षम बनाती है।

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Nomenclature

Symbol	Definition
b	Kuhn monomer size
f_i	Volume fraction of i^{th} block of a block copolymer chain
h	Planck's constant
k_B	Boltzmann constant
n	Total number of polymeric chains in the system
n_f	Number of free polymer chains
n_g	Number of grafted polymer chains
q_i	Forward chain propagator of species i
q_i^\dagger	Backward chain propagator of species i
s	Parameter indexing the segments along the chain contour
$u_{\alpha\beta}$	Dimensionless pair potential between polymeric segments α and β
v_0	Monomer volume
D	Distance between two clay nanosheets
F	Helmholtz free energy of the system
H	Surface potential field due to confinement
L	Length of clay nanosheet or length of nanopore
N	Degree of polymerization of a polymer chain
N_a	Degree of polymerization of a dangling arm in grafted star molecule
N_f	Degree of polymerization of a free polymer chain
N_g	Degree of polymerization of a grafted polymer chain
N_s	Degree of polymerization of a grafted star molecule
Q	Single chain partition function
R	Radius of circular confinement
R_g	Radius of gyration of matrix polymer chain
R_p	Radius of spherical nanoparticle

T	Temperature of the system
V	Volume of the periodic box
V_p	Volume occupied by the polymer
W	Width of clay nanosheet
U_0	Elastic potential energy of a Gaussian chain
U_1	Interaction potential energy of a Gaussian chain
Z	Partition function for canonical ensemble

Greek Symbols

Symbol	Definition
α	Ratio of the volume of particle core to volume of the copolymer chain
β	Size ratio of the grafted and block copolymer chain in matrix
χ_{ij}	Flory's pair interaction parameter between species i and j
ϵ	Selectivity of particle core to the polymeric species
γ_f	Number of arms in a free star molecules
γ_g	Number of arms in a grafted star molecules
κ	Cut-off distance for interaction with confining wall
λ	Domain periodicity of ordered phase in bulk
ω_i	Potential field experienced by species i
ϕ_i	Local volume fraction of species i
$\bar{\phi}_i$	Average volume fraction of species i
ρ_0	Number density of a Kuhn monomer ($\rho_0 = 1/v_0$)
ρ_i	Density field of species i
$\hat{\rho}_i$	Microscopic number density field of species i
σ	Measure of grafting density
τ	Characteristic decay length for interaction potential with wall
ζ	Incompressibility (pressure) field