MATERIALS SCIENCE

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Metallopolymer Nanocomposites

Springer

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With 239 Figures

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To the memory of our fathers Dmitriy Ivanovich and Nikolay Yakovlevich,
participants in World War II and great toilers, with hope that our children
and grandchildren will be deserving of their memory

Foreword

The way from the micrometer to the nanometer scale is a further step in the miniaturization of active particles and functional components for technical applications. Physical and chemical properties change due to the occurrence of size-dependent quantum and confinement effects. Ceramics may become transparent like glass; glass can become tough like adhesive; metals may become coloured like dyes; magnetism can be switched on and off, etc. In order to understand this behaviour, fundamental research is necessary. In addition, it can be foreseen that nanomaterials and their technology will be one of the most important technologies of the 21st century.

The kinds of materials addressed are, in principle, the same as those encountered in macro- and microtechnologies. Examples are polymers, ceramics, metals, semiconductors, and insulators. But in place of the top-down approach, the bottom-up approach now becomes the key to devising new, for example, composite or hybrid materials. Nanotechnology exploits the same building blocks and structural elements as other technologies: atoms, molecules, solids. But the difference to the classical materials is that the structural elements consist of small and sometimes very small ensembles of atoms and molecules. In the classical case the number of surface atoms or molecules is small compared to the number of bulk particles. In the case of nanomaterials this situation is reversed.

One of the most important materials for future nanotechnology will be metal nanoparticles, due to the very unusual properties that they display. After some decades of fundamental research in this field, a summary of the state of the art is of great value. The monograph of A.D. Pomogailo and V.N. Kestelman is the first book that compiles detailed information about metallopolymer nanocomposites. These are entities that involve a combination of metal nanoparticles and macromolecules. Two excellent and well-known scientists have taken up the challenge and provided this detailed overview.

Before discussing the fundamental role of the polymer, the text first addresses stabilization of metal nanoparticles, fundamentals in classification/organization and nucleation mechanisms. The chapters about synthesis methods include all details about physical, chemical and physico-chemical procedures for the synthesis of metal-polymer nanocomposites. Polymer-inorganic nanocomposites (sol-gel processes, intercalation hybrids, nanobiocomposites) are also described. Special attention is paid to properties and many applications are described. A large number of references will help readers to gain a more-detailed acquaintance with almost all the details and problems involved in research into metallopolymer nanocomposites. I am sure that this excellent book will be a great success and an important contribution to furthering the field of nanoscience and nanotechnology.

University of Bremen, Germany *Dieter Wöhrle*
January, 2005

Preface

By the end of the twentieth century, considerable success in nanochemistry and nanotechnology had been achieved. As a result, two novel scientific areas of nanosize chemistry and functional materials science have appeared. The nanoworld is a world of quantum coherences and nonequilibrium processes of self-organization. Nanoparticles (with sizes in the range 1–100 nm) are at the boundary of the classic and quantum worlds. At present, great progress is being achieved in these investigations.

New properties of nanoparticles, nanolayers, superlattices and metal–polymeric composites have been discovered, and these are of great interest as very promising materials for microelectronics, holography and magnetic recording of information. This monograph deals mostly with the logic of investigations and the inner methodological and scientific interconnections in the field. It is hardly possible to present a survey of the whole of polymer nanocomposite science taking place throughout the world. This science is continually developing and many principal results and their interpretations are being revised. There are many reviews and books about specific properties, technologies and applications of nanomaterials; we have decided to devote this book to the basics of the science of metallopolymer nanocomposites. This is the first book of this kind, summarizing the results of more than 30 years of research in this area, from the technology of nanoparticles, problems of stabilization, and immobilization in the polymer matrix, to design of nanohybrid polymer–inorganic nanocomposites and different applications of these materials.

This book reflects the present state of the problems considered, and many ideas are still being elaborated. However, certain materials and structural aspects, and also biological problems, are not considered in detail here.

We hope that the book will be of interest to experienced and young specialists in nanochemistry and nanophysics.

Our thanks go to colleagues who supported this book, mostly to Profs. Dieter Wohrle, Franz Faupel, David Avnir, Kennett Suslik, Robert E. Cohen, Mercouri Kanatzidis, Ulrich Schubert, Dominique Bazin, Ralf Zee, Sergey Gubin, Rostislav Andrievskii, etc. Our colleagues in the laboratory have carried out a large number of experiments, most of which are represented in this book. Prof. Aleksander Rozenberg did his share for Chaps. 2 and 11 and

offered his valuable remarks. Dr. Gulzhian Dzhardimalieva has made an important contribution to the synthesis of metallopolymer nanocomposites by polymerization of metal-containing monomers. We would like to express our special appreciation of her enormous help and contribution to this book.

Undoubtedly, as usual for a first multidisciplinary monograph, there may be room for improvement. We would greatly appreciate any comments and suggestions.

Chernogolovka, Russia, KVN International, USA
January, 2005

Anatolii Pomogailo
Vladimir Kestelman

List of Abbreviations

A	Hamaker's constant
AcAc	acetylacetone
AFM	atomic-force microscopy
AIBN	azobis(isobutironitrile)
AOT	bis(2-ethylhexyl) sulphosuccinate
ATP	adenosine triphosphate
ATRP	atom transfer radical polymerization
C_m	volume concentration
Cerasomes	organoalkoxysilane proamphilites
COD	cyclooctadiene
CSDVB	copolymer of styrene with divinylbenzene
CVD	chemical vapor deposition
D	diffusion coefficient
D	fractal dimensionality
D_s	fractal dimensionality
Dipy	dipyridyle
DMAAm	N,N-dimethacrylamide
DMFA	dimethyl formamide
DMSO	dimethyl sulfoxide
DNA	deoxyribonucleic acid
EDTA	ethylenediaminetetraacetate
ESCA	electron spectroscopy for chemical application
EXAFS	extended X-ray absorption fine structure
FC	fractal cluster
Fe_3O_4	magnetite
Fe_3S_4	greigite
FMR	ferromagnetic resonance
FTIR	Fourier transform infrared spectroscopy
HDPE	high density polyethylene
HEMA	2-hydroxyethyl methacrylate
HOPG	highly oriented pyrolytitic graphite
HSA	human serum albumin
HTSC	high-temperature superconducting ceramics
IPN	interpenetrating polymer networks
ITO	indium tin oxide electrode

L	ligand
LB	Langmuir-Blodgett films
LCG	layered interstitial compounds in graphite
LCST	low critical solution temperature
LDLPE	low density linear polyethylene
LDPE	low density polyethylene
M_j	nanoparticle consisting of j atoms
MAO	methylalumoxane
MC	Monte Carlo method
MCC	micelle-forming critical concentration
MCM-41	hexagonal materials (Mobil codes)
MCM-48	cubic materials (Mobil codes)
MMA	methylmethacrylate
MMD	molecular-mass distribution
MMO	methane monooxygenase
MMT	montmorillonite type clays
$MO_n(OR)_m$	oxoalkoholates
MRI	magnetic resonance imaging
MX_n	metallocomplex
(MV^{2+})	methylviologene (dimethyl-4,4-bipyridine)
NADH	nicotine-amide reduced
NC	coordination number
NLO	nonlinear optical
NP	nanoparticle
NVI	N-vinylimidazole
OGC	oxygen-generated center
ORMOCER	Organically Modified Ceramics
ORMOSIL	Organically Modified Silicates
P	cross-linked polymer
P*i*PA	poly(N-*iso*-propylacrylamide)
P2VPy	poly(2-vinylpyridine)
P4VPy	poly(4-vinylpyridine)
PA	polyamide
PAA	poly(acrylic acid)
PAAm	poly(acrylamide)
PAMAM	polyamidoamine (dendrimer)
PAn	PANI polyaniline
PAN	polyacrylonitrile
PB	polybutene
PBD	polybutadiene
PBIA	polybenzimidazole
PBIA	polyheteroarylene
PC	percolation cluster
PCL	poly(ε-caprolactone)
PDMS	poly(dimethylsiloxane)

PE	polyethylene
PEO	polyethylene glycol
PE-gr-P4Vpy	polyethylene grafted poly(4-vinylpyridine)
PEI	polyethyleneimine
PEO	polyethyleneoxide
PES	polyestersulfone
PETP	polyethylene terephthalate
Phen	phenantroline
PhTMOS	phenyltrimethoxysilane
PI	polyisoprene
PM	polymer matrix
PMAAc	poly(methylacylic acid)
PMMA	poly(methylmethacrylate)
PMPhSi	poly(methylphenylsilane)
PMVK	poly(methylvinyl ketone)
POSS	polyhedral oligosilsesquioxane-based macromers
PP	polypropylene
PPG	polypropylene glycol
PphO	poly(2,6-dimethyl-1,4-phenylene oxide)
PPO	polypropyleneoxide
PPy	polypyrrole
PS	polystyrene
PSE	polymeric solid electrolytes
PTFE	poly(tetrafluoroethylene)
PU	polyurethane
PVA	poly(vinylalcohol)
PVAc	poly(vinyl acetate)
PVB	poly(vinylbutyral)
PVC	polyvinylchloride
PVDC	poly(diallyldimethyl ammonium chloride)
PVIA	poly(1-vinylimidazole)
PVK	poly(vinylcarbazole)
PVP	poly-N-(vinyl-2-pyrrolidone)
Py	pyridine
QD	quantum dots
S_{sp}	specific surface
S	solvent
SAS	surface active substance
SAXS	small-angle X-ray scattering
SCA	specific catalytic activity
SEM	scanning electron microscopy
S-layers	surface layers
SSA	specific surface area
STM	scanning tunnel microscopy
TEM	transmission electron microscopy

TEOS	tetraethoxysilane
T_g	glass transition temperature
TGA	thermal gravimetry analysis
THF	tetrahydrofuran
Ti-MCM-41	Ti-materials (Mobil codes)
T_m	melt temperature
TMOS	tetramethoxysilane
TN	turnover number of catalyst
t-RNA	t-ribonucleic acid
XPS	X-ray photoelectron spectroscopy
ZSM-5	zeolites
(α, β and γ)-PP	crystal form of isotactic PP
γ-Fe_2O_3	maghemite
φ_{cr}	volume portion of filler
4Vp	4-vinylpyridine

Contents