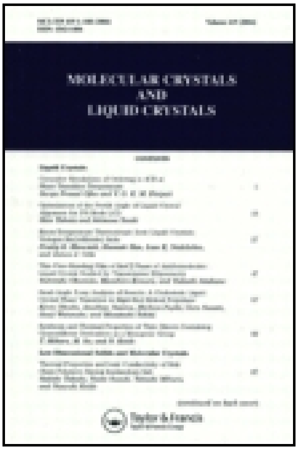

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From Microcrystals to Nanoparticles in Heterogeneous Polymers

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From Microcrystals to Nanoparticles in Heterogeneous Polymers

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Methods of preparation and properties of composites of micro and nanoparticles with polymers are reviewed. Attention is paid particularly to electrical, optical and related properties. Some nanostructured systems are discussed in more detail. The short discussion of nanointercalates is presented to show the correlations between these two types of nanosystems. The discussion is closed with author's personal view on some aspects of nanoscience in terms of nanocomposites.

Keywords: nanocomposites; nanointercalates; nano-structure related properties

INTRODUCTION

There is a great need for new materials, which are constructed of small blocks of nanometer size. The specific architecture of such systems is determined by the complex interplay among building blocks and interfaces between them. It is like in the living matter, which is an unattainable model of very complex and unique structures of various hierarchies. One should try to mimic the Nature. At first inorganic nanocomposites have created huge interest because of their unique mechanical properties.

Nanocomposites can be classified into several broad categories:
a) ceramic/ceramic b) metal/ceramic c) ceramic/polymer d) polymer/low molecular weight compound e) immiscible polymer blends
We will our focus attention particularly on organic microcrystallites and nanosystems in polymers. Preparation processes of ultrathin organic films or a micro- and nano- block includes two techniques: 1. dry techniques which are related to: a) chemical vapour deposition (CVD) in different variants, b) sputtering, c) organic molecular beam epitaxy (OBME) 2. the "wet" techniques are of increasing importance: a) Langmuir-Blodgett method is still very

interesting to obtain nanocrystals and nanocomposites, b) self-assembled monolayer (SAM's) method has been developed to high degree of sophistication to produce supermolecular architectures. It is accepted by many researchers and is one of the basic mechanisms to study the molecular interactions and fabrication of various devices, c) specific crystallisation of organic compounds *in situ* of polymer matrix by evaporation of common solvent lead to reticulated doped polymers and related techniques (RDP).

RETICULATED DOPED POLYMERS

This method was developed by us [1-3] for obtaining conducting polymer films consisting of organic metals – i.e. strong CT complexes and/or complex salts and inert polymer matrices. There are two general ways of RDP's preparation methods. The first-one-step method consists in inducing crystallisation of the CT complex *in situ* in the system composed of a donor, an acceptor, a polymer and a common solvent. The controlled evaporation of the solvent leads to isotropic systems. The particularities of this method consists in very low percolation threshold for huge increase of conducting network (below 0,003 volume fraction of the CT complex e.g. TTT- TCNQ (tetrathiotetracene and tetracyanoquinodimethane) in polycarbonate (PC) [4]. Thus mechanical properties are preserved

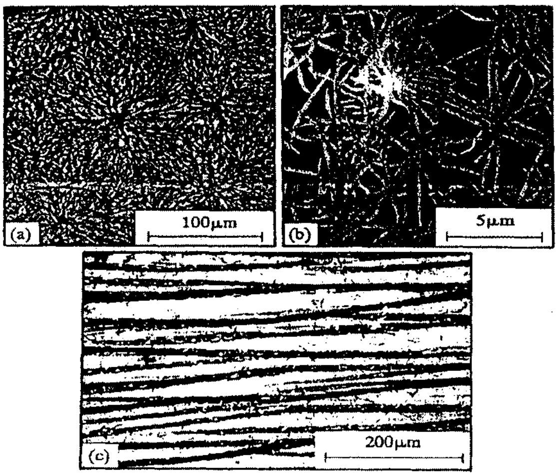

FIGURE 1 a) Micrograph of the bulk conducting film of PC reticulatiate doped with 1wt % of TTT-TCNQ (cast from o-dichlorobenzene, b) scanning electron micrograph showing the morphology of the conducting crystalline network of (a). Micrograph of anisotropically film of PE (polyethylene) containing 1 wt% of TTT$(TCNQ)_2$ obtained by zone casting technique (c) [2,6].

. It was shown that amorphous and semicrystalline polymers can be used as matrices as well as more than 30 CT complexes and complex salts have been successfully applied as conducting phases. Depending on the crystallisation conditions that govern the morphology of the network [5] one can fabricate polymer films, which show different electrical properties i.e. a) isotropic, b) anisotropic and c) surface conductivity. The different structures of the conducting phase in polymer films are presented in Fig.1.

The macroscopic anisotropy of the conductivity is expressed as $\delta_{II}/\delta_{I} \approx 10^7$. High voltage EM micrograph of isotropic TTT-TCNQ in polycarbonate matrix shows very clearly the nanoscopic nature of the fine structure of the conducting network [7].

FIGURE 2 High voltage EM micrograph of the structure of RDP

Conductivity of this network was displayed by d.c. and a.c conductivity measurements [8]. The magnetic properties of these systems have been investigated too (see e.g. Jeszka [9]) giving with before mentioned studies a penetrating description of these nanostructured materials (with exception of anisotropic systems which consists of microcrystalline "strings". A two step method is used to obtain surface conducting films (and under appropriate conditions also volume-conducting films). Molecularly dispersed CT complex in solid polymer matrix is exposed to vapours of a solvent or solvent mixture. The solvent induced polymer chains mobility and at the same times the crystallisation of the CT complex at the surface yielding the surface conducting films. One should to mention that there are two variants of fabrication surface conducting films. The first consists in exposal the molecularly dispersed one component of the CT complex to a swelling agent and simultaneously treating with another CT-complex component. The second method consists in thermal treatment of a polymeric matrix containing molecularly dispersed CT-complex (the matrices of Tg below the decomposition temperatures of CT-complex e.g. polyacrylates) [10-12].

The two step technique was used to obtain micro-polycrystalline surface layers of bis-ethylenedithia(tetrafulvalene)(ET) with polyiodides within polymer matrix. This material is superconducting thus obviously present a great interest [13]. The compactness of the text does not allow to give detail the preparation of these superconducting films, which have some advantages as compared with single crystals of (ET) polyiodides. The objective of this discussion is to show the micro- or nanocrystalline structure of all theses systems. There are three different kinds of structures of ET_2I_3 as detected by X-ray diffraction studies: α-ET_2I_3, β-ET_2I_3 and ET. The morphology of microcrystallites and the relative content of both ET_2I_3 phases and neutral ET can be controlled by I_2 concentration during vapour treatment and duration of this treatment [14] and references therein.

Films with ET polyiodides showing superconducting properties undergo phase transformation of α-ET_2I_3 into β-ET_2I_3 (which is superconducting) by annealing at 430K [13]. The studies of Tracz [15-16] concerning the structure of ET_2T_3 microcrystallites on the surface layers of above mentioned films have shown interesting results in respect to their nanosize dimensions. By means of SEM one sees structureless almost continous layer (flack like morphological structures). Using nanoscope (tapping mode) layered nature of flackes appears distinctly. At still higher magnification one can observe step highs, which corresponds to the interlayer distance in α-ET_2I_3. Fig 3 shows β-$(ET)_2I_3$ structure

FIGURE 3 Structure of nanocrystallites of β-$(ET)_2I_3$

These very convincing results have been obtained from the section analysis of these microcrystallites. Fig. 4 shows surface roughness of one of the β-ET_2I_3 nanocrystallites. The clear side slip on the graph 3a is seen which corresponds to vertical distance 14.563 nm indicated by two arrows.

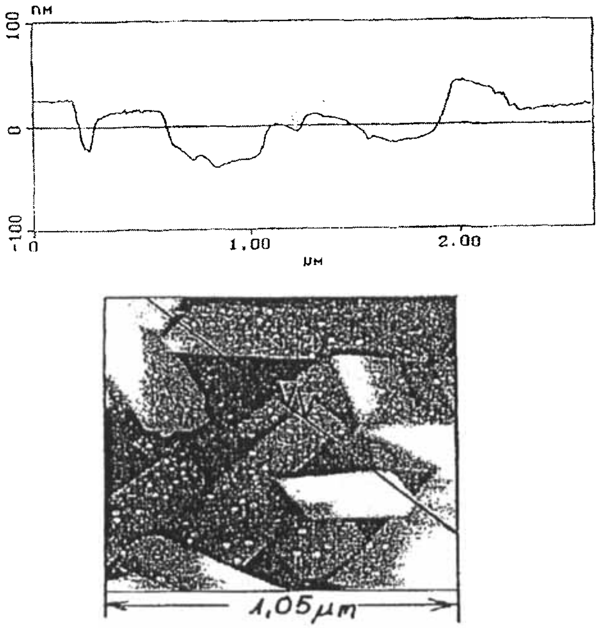

FIGURE 4 a) Section analysis of the surface of microcrystallites of β-ET_2I_3, b) the micrograph of the surface of β-ET_2I_3 indicating the direction nanoscan

The analysis presented above shows that the RDP systems, both conducting and superconducting, are composed of nanocrystallites in polymeric matrices. The structured additives exhibit interesting electrical properties, which are well controlled by the composition and the preparation conditions.

MICROCRYSTALLITES AND NANOPARTICLES IN POLYMERS

Some aspects of micro- and nanocrystallites in polymer have been discussed by us before [17,18]. Basic concepts will be only repeated briefly and new results on the role of nanocrystals in polymeric matrices will be represented. It worth while to stress that very small particles can be considered as nanoparticles when at least one of the dimension will be of nanosize. It concerns also nanolayers. Very small microcrystals of TCNQ salts with alkali metals in the ratio 1:1 were prepared. These microcrystals as well as those with triethylammonium TEA were obtained by one of our methods of formation microcrystallites *in situ* of polymer matrix. Solid solution of CT salts in PMMA (poly(methyl methacrylate) were exposed to solvents vapours or (heat treated) [19]. The strong dependence of lowest electronic of alkali metal salts states on crystallite size and CT-bands have been described. Non-linear refraction of heat-treated films containing TEA is reported too. It is in some relation with the nanostructural non-linear optical conjugated systems described in paper [18]. In the last mentioned work three types of heterogeneous materials for non-linear optics were obtained: a) the interdispersed materials, b) layered systems, c) dispersion. All these three composites are nanosystems. For the sake of the compactness of the text it is necessary to give up the details on these systems. The interdispersed materials are composed of micro particles of different dielectric constants ε_1 and ε_2 a packed densely thus leading to dielectric confinement. Dielectric confinement consists in the in the concentration of electric field lines in certain region of heterogeneous material. The optical properties are therefore changed thus the optical constants of the region where the field lines are confined in different form the average properties of the material.

Our interest in nanoparticles went through the study colloidal particles from the viewpoint of their packing in order to "experimental simulation" of formation molecular crystallites [20]. Poly(styrene co-acrolein) (PSA) latex with aldehyde groups on the surface, could be immobilised of the quartz surface modified with γ-aminopropyl trietoxysilane, forming the two-dimensional assemblies. The degree of coverage of quartz surface and the morphology of immobilise latex assemblies could be controlled by varying conditions of the modification of quartz surface and of incubation with suspension of PSA latex. Computer simulation demonstrated that very fast covalent immobilisation of particles results in the very low degree of coverage. In the case of slow covalent immobilisation the large crystal-like structures would be formed. These systems are not true nanosystem but their studies gave us an experience to investigate real nanoparticles in polymers [21].

The specific class of nanosystems is the dispersions of metal or semiconductor nanoparticles in polymers. We have to leave out an account of metal nano-clusters fabricated directly e.g. by vacuum deposition. They still are of great interest. It is known that physical and optical properties of small metal particles in transparent media depend on particle kind, size and distribution. There is well-advanced physics of optical properties of nanoparticles in transparent media thus it seems not necessary to discussed this type of properties of nanosystems. Evidently a huge progress in this field has to be noticed.

Less known is the influence of metal nanoparticles on mechanical behaviour of such nanocomposites. Our recent studies concerned the mechanical properties-Young modulus of palladium nanoinclusions. For our studies we selected poly[methyl-acrylate](PMMA)-palladium(Pd) nanocomposite [22]. We will not go into the preparation of samples. There are many empirical equations which describe the Young's modulus of the composite which contains the values of: Poison ratio v, elastic modulus of the matrix E_0, elastic modulus of the filler E_f and measured elastic of the composite E_c and Φ the volume fraction of the filler. It was shown that the real volume of Pd-nanoparticles should be substituted by effective filler volume $\Phi=\Phi_0(1+\Delta R/R)^3$ where ΔR is the increase of the nanoparticle radius R which was determined by direct EM measurements of the Pd-nanoinclusions. The studies concerned the nanocomposites in the range zero to 0,012 whereby radius of Pd-nanoparticles was in the concentration range 1 to 2nm. The increase of the effective radius $(R+\Delta R)$ can be explained by immobilisation of the matrix in the environment of Pd-particles. It is due to the reaction on the fresh surface of Pd-nanoparticles formed *in situ* during the preparation of the nanocomposite. These results show that even a small content of nanoinclusions influences the mechanical behaviour of glassy polymers.

The preparations of organic nanocrystallites have attracted little attention because of difficulties related to their preparation and characterisation. The dry techniques (vacuum deposition) are elegant but have some drawbacks and require expensive equipment. Recently novel wet technique [23,24] was elaborated. It consists in reprecipitation of an organic compound from its solution (in a form of emulsion is non-solvent). The reprecipitation occurs in very small droplets in the nonsolvent by vigorous stirring (e.g. water). This treatment results in formation small liquid particles in which the concentration of solvent decreases thus nucleation and crystallisation takes place in confined volume. Small crystallites are separated and show some physical properties characteristic of nanosized solids. Sol gel technique was also used to prepare organic nanocrystals of many substances, several of them showing non-linear properties [25]. It should be mention that the property differences of nanocrystallites of organic solids are not as clear as in the case of inorganic nanocrystals. It is due to the fact that organic molecules which show interesting electrical or optical properties are relatively big, as compared nanoscopic crystals, contains small number of molecules thus the influence of size has somehow different nature. Organic molecules form molecular crystals in which intermolecular forces are weak and therefore surface effects are also relatively not well expressed. In our recent work [26] nanocrystals of (ET) polyiodides in polymeric matrices were obtained by different methods of crystallisation under limited diffusion conditions [27,28]. Broadening X-ray diffraction, atomic force microscopy confirms decreasing size of crystallites. UV-spectra are not changed very much but IR spectra show a small CT band shifts as compared with microcrystalline layers. Raman spectra confirm that above 300K α-ET_2I_3 is formed in contrast to β_ω-ET_2I_3 phase microcrystals formed above 370K in solution [29,30].

SUPERPARAMAGNETIC NANOPARTICLES IN DIELECTRICS AND CONDUCTING POLYMERS

The interest in superparamagnetic composites increases continually both from scientific and application view points. It seems on purpose to remind the basic arrangement of atomic spins in three kind of magnetic materials.

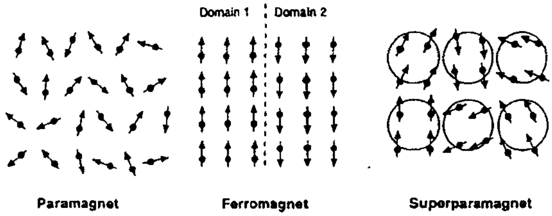

FIGURE 5 Schematic representation of arrangement of atomic spins, which define magnetic properties

Superparamagnetism arises as the result of magnetic anisotropy, spins are aligned along preferred crystallographic directions. When the energy is increased magnetisation can be reversed along these axes. The relaxation time τ depends on the high of the energy barrier which separates forward and reverse states $\tau \sim \exp(K_{eff}V/KT)$ where K_{eff} is anisotropy constant, V is particle volume, K-Boltzmann constant and T-temperature in K. If the relaxation time at given temperature is short the direction of particles changes spontaneously and the particles behave as superparamagnetic particles. Such particles stick to the magnet but not to each other. They are magnets in magnetic field. Superparamagnetism can be observed at room temperature for iron oxide particles of the order of 10 nm. We have to live out an account of the theory of magnetic properties of superparamagnetic nanoparticles. All parameters needed for calculation of magnetisation M vs magnetic field H can be easily obtained experimentally from characteristics of such nanoparticles.

Nanosized paramagnetic particles in polymers (nanocomposites) constitute new strategy to obtain complementary behaviour between the polymer and inorganic solids interacting on molecular or quasi-molecular level. Several kinds of nanosized paramagnetic particles have been incorporated into various polymers. The limiting factor in the studies and application of such systems (e.g. as cooling devices) is usually nanoparticles aggregation. Fine dispersions, without important aggregation, can be achieved by formation of such particles *in situ* or by the use of ferromagnetic fluids in specific conditions [31]. Ziolo et all [32] obtained a composite of nanometer ferric oxide (γ-Fe_2O_3) particles in polymeric commercial ion-exchange resin. The details of preparation of such composite are given in [32]. It is interesting to note that the Fe content of the order 40% was obtained whereby particles had a diameter at about 10 nm (much less then those used in magnetic types. The role of the polymer matrix is minimising the aggregation and to promote the formation of γ phase of Fe_2O_3. The measured saturation magnetisation M is by about 10% lower than expected on the basis of iron content and the value of the bulk γ-Fe_2O_3. The difference is attributed to the small size of superparamagnetic particles but no detailed information is given.

Small particles of γ-Fe_2O_3 are more transparent than other magnetic materials at room temperature thus they are the objective of some studies but interpretation of optical measurement results demands particular attention. A rather small number of papers have been devoted to various metal oxides and semiconducting particles in polymers. Most of them concerned heterogeneous conducting polymers e.g. polypyrrole [33-36] We have investigated superparamagnetic particles in polyaniline (PAni) [31].

The objective of this research concerned the explanation of the decrease of the saturation magnetisation in the composites, as compared with bulk single crystal of iron oxides. We have selected the system PAni/iron oxide because the interaction of various components used in superparamagnetic nanocomposite preparation can be well investigated and controlled. We thus expected to throw some light on this open question. The counterions in the composite can also influence its morphology, because the iron oxide particles have been introduced as a ferrofluid. It seems interesting to note that the specific condition of preparation, the chemical structure of doped PAni and its morphology may influence the interactions at the γ-Fe_2O_3 or Fe_3O_4 nanoparticles. The IR spectra were analysed in order to investigate the surface of the oxide particles. The IR spectra are shown in Fig. 6.

We will leave out the detailed description of the IR spectra presented in Fig. 6 and only concentrate on some characteristic features.

The bands at 1578, 1942 and 1302 cm^{-1} attributed to -C=C- bonds in quinoid structure (Q), phenylene rings, (B) and C-N bonds respectively, are shifted to lower wave lengths as compared with "pure" PAni. See the scheme of PAni chemical structure given in Fig. 7.

To cut the story short one can conclude though that during aniline, polymerisation [31] iron oxide particles are partially reduced and they act as compensating agents for doped PAni chains. This results in strong interaction with the nanoparticle surface. The increase of the intensity at the 1168 cm^{-1} corresponds to vibrations of C-N bonds in Ph-NH-Ph groups (B). Magnetisation studies of the system PAni/iron oxide have shown that nanocomposite containing superparamagnetic particles do not exhibit histeresis. The fit of the magnetisation M *vs* applied magnetic H field curve allows for calculation of all parameters related to M_0=f(H) (with consideration of particle size and concentration etc. The calculated anisotropy coefficient K_{eff} is 0,7 of that expected for bulk superparamagnetic iron oxide. This explains why there are deviations from $M/M_0=1$. They are due to interactions of fragments of PAni chains (or intermediates).

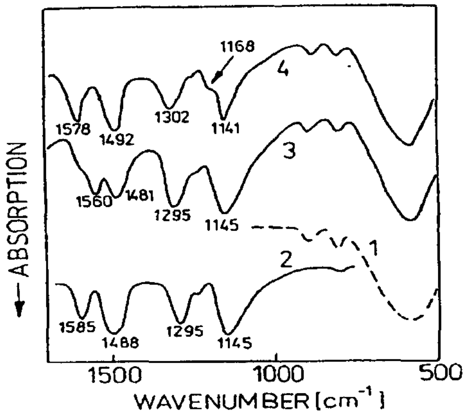

FIGURE 6 IR absorption spectra of PAni/Fe$_3$O$_4$ nanocomposites (curve 4, doped PAni; curve 3, undoped PAni), compared with those of PAni/HCl (curve 2) and ferrofluid (curve 1)

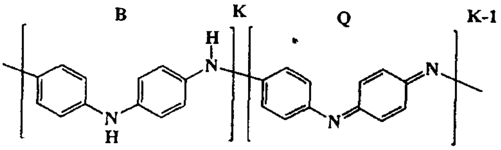

FIGURE 7 Schematic presentation of polyaniline structure

This also is seen in the IR spectra. It seems that these observations are general for all known superparamagnetic, composites of conducting polymers as well as for other metal, metal oxides and semiconductor particles. These results show how important are the interaction forces at the specific and characteristic interphase of such kind of nanocomposites. We hope that these studies will be further developed because of their importance for science and technology.

Evidently this general analysis concerned some selected examples of preparation and properties nanoparticles in polymers. There is a wealth of experimental evidence and theoretical discussion of various nanosystems e.g. these which were nanoscopically engineered taking also into consideration their processing.

NANOINTERCALATES

In designing new nanocomposites should take into consideration layered inorganic solids which can act as host lattices for organic and inorganic guests. A great number of papers, which can not be quoted here, have been devoted to intercalates. Recently we have presented a concise review of very interesting problems related to preparation and properties of nanointercalates [37]. The term intercalation is used to describe insertion of mobile guest species (atom, ion molecules and macromolecules) into crystalline lattice, which must contain empty sites or empty space between weakly bound layers. The ample knowledge on the intercalates is general helps to select the strategy to obtain a guest polymer within the given host crystal or micro- and nanocrystalline guests in a polymer. To introduce polymers or other organic molecules between the layers of host it has to be usually delaminated or exfoliated. Let us give some examples. The pioneering work of Giannelis [38] concerned polymer melt-intercalated silicates (e.g. montmorillonite) is shown schematically on Fig. 8.

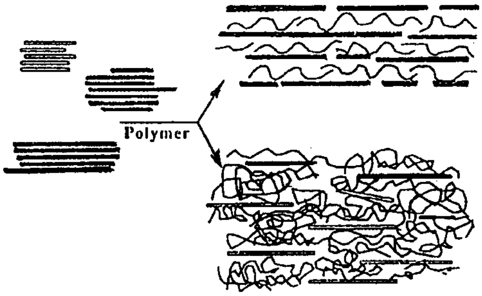

FIGURE 8 Scheme of intercalation of polymer into layered silicate

One can obtain an intercalation of single polymer chain between the layers of silicate or a dispersion of thin nanoscopic layers in polymeric matrix. These structures exhibit evidently different mechanical and thermal properties being a model for attempts to prepare nanointercalates with interesting electrical and optical properties. One has to consider to the class of nanointercalates the thin nanocrystallites of conducting and superconducting compounds in polymeric matrices. They were discussed before. Transition metal dichalcogenides hosts are very popular e.g. TiS_2 or MoS_2. Exfoliation of MoS_2 is more complicated but they have been used to prepare nanolayered composites with poly(phenylene vinylene) [39]. In correlation with remarks given before it seems on purpose to indicate here the nanointercalation of polyaniline into MoS_2 [40] which is schematically presented in Fig. 9.

The above presented examples and are a selected birth-view of some intercalates aiming particularly to show the close structural aspects of nanocomposites and nanointercalates. At the end of this discussion one should stress the contribution of chemistry in the selection guest and host. It determines the properties of nanointercalates. Physicists often underestimate it and engineers may be with exception of those who are working in the field of non-linear optics and molecular electronics.

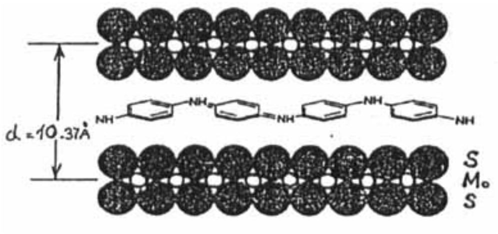

FIGURE 9 Scheme of lamellar structure of intercalates $(PAni)_{0,35}MoS_2$ (redrawn after[40])

CONCLUDING REMARKS

The review of such type can not be summarised in "pioints". The idea of getting molecules together to make order and specific structures is mimicking the Nature, which is always composed of perfect building blocks and their perfect arrangement.

Before giving some personal remarks on the future development of the nanoscience, particularly in the area of nanocomposites, it is necessary to indicate that the roots of methods of preparation and characteristics such nano-materials are deeply connected with the wide and growing field of self assemblies and with colloid chemistry.

The goal of this part is to present some concepts on the future of nanocomposites and nanointercalates. Nanomaterials (structure and properties) have been discussed at numerous international symposia dedicated to scientific or application aspects of such composites as well as in many books. These works show that progress in that interdisciplinary field needs an intense concentration.

It seems that research on nanomaterials has been stimulated by their applications (catalysts, pigments etc.). The technologically useful properties of nanomaterials are not limited to their structural, chemical or physical behaviour, which can not be discussed here even briefly.

Confinement of electrons to small geometries give rise to "particles in box" energy levels which result in the modification on optoelectronic properties of semiconductors (microelectronics) reduction of the melting temperature and changes in the lattice parameters (structure). The studies in that direction will be continued and one can expect that they will result in new concepts for new devices.

Research on nanomaterials has lead to formation of new fields such as discovery, large production of C_{60} and related compounds, which are still very attractive.

Nanoparticles have to be consolidated under vacuum or by dispersions in other materials particularly in polymers. These types of nanocomposites have been discussed before but, by no means, this field is adequately described. There are numerous problems to be solved, which will lead to new materials with extraordinary properties to follow the concept: "life itself could be regarded as a nanophase system". The knowledge of the immobilisation of nanoscale particles and clusters in polymeric matrices is still not sufficient.

New instrumentation techniques (STM) and (ATM) and other probes provide new possibilities to characterise nanoparticles and to more advantageous use of their properties in various kind of assemblies.

A variety of computational methods have been used to perform theoretical studies of the properties on nanoparticles but the theory of cluster formation needs more effort (approximate methods *vs* first-principle calculations).

These brief personal remarks can be closed with perfect formulation of Sir Cyril N. Hinshelwood in his Centenary Address to the Chemical Society [41]:

> *"Chemistry provides not only a mental discipline, but an adventure and an aesthetic experience. Its followers seek to know the hidden causes which underlie the transformations of our changing world, to learn the essence of the rose's colour, the lilac's fragrance, and the oak's tenacity, and to understand the secret paths by which the sunlight and the air create these wonders. And to this knowledge they attach an absolute value, that of truth and beauty. The vision of Nature yields the secret of power and wealth, and for this it may by sought by many. But it is revealed only to those who seek if for itself."*

These words apply fully to Physics, which is the Older Sister of Chemistry.

Acknowledgements
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