Oxidation of pyrolized polyacrylonitrile carbon nanostructures

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Polyacrylonitrile is one of the most promising polymers as it is widely spread and can be applied in various fields. However, the properties of the pyrolized polyacrylonitrile (PAN) are not studied well by now. One of the major features of it is the ability of pyrolized polyacrylonitrile monolayer to accumulate different atoms.

The calculation of oxygen atom adsorption process has been done within the model of ion-embedded covalent-cyclic cluster (IE-CCC) based on the semiempirical quantum chemical calculation system, called MNDO. This calculation method is chosen because the results of previously made analysis of some highmolecular solid-state structures go closely with our experiment. Bonding of oxygen atom to carbon atom from the monolayer surface of pyrolized polyacrylonitrile (PPAN) is examined.

Step-by-step approximation of adsorbed oxygen atom towards PPAN monolayer allowed us to build a system potential energy surface "PPAN – oxygen atom" (dependence of energy on R_{C-H} distance between oxygen atom and carbon atom on the surface). Further analysis of this dependence let us determine the distance of formation of chemical bonds between oxygen atoms and carbon atoms on the PAN surface. It happens due to overlap of C and O atomic orbitals and following electron density exchange.

System geometry optimization analysis has revealed the fact, that adsorption of elemental oxygen on the PPAN monolayer surface leads to its deformation. Moreover, the adsorbing carbon atom lifts a little over the monolayer surface and the neighboring atom lowers and goes inside thus forming additional active center from the other side of the monolayer.

Investigation shows, that monolayer oxidation through periodic adsorption of several O atoms on the PPAN surface leads to system binding energy degradation. Moreover, after oxidation of more than 11% of all monolayer surface atoms, the PPAN monolayer collapses.

Structure and vibrational spectra of multi-walled carbon nanotubes with the polypropylene during irradiation

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The composites of polymers with the carbon nanotubes (CNT) lead to a substantial change in the mechanical, transport and optical properties of polymers. The influence of the polymeric molecules on the CNT is studied less. It is obvious, that the nature of the transformations of the CNT physical properties depends on the presence of interaction between the molecular chains and the CNT, i.e., from the hybridization of their electronic states. The presence of this hybridization must be especially noticeable on the behavior of D band and two-phonon scattering D *, which corresponds to this band. Furthermore, the presence of sp³ hybridization must contribute to the crystallization of polymers and disordering of CNT because of the defects formation. To a greater extent the transition from sp^2 hybridized states of CNT to sp^3 states must grow under irradiation, which facilitates the radiation defects formation. However, with an increase in the fluence of irradiation an increase in the annealing rate of these defects should be expected. Therefore, to foresee previously the irradiation effect on the nature of interaction between the polymeric molecules and CNT is difficult. It can be established only during the study of the transformation of the polymer crystalline phase and vibrational modes at the beginning and on the boundary of Brillouin zone for the CNT, connected with D and D * bands. In the present work the composites of polypropylene with different content of multi-walled CNT were investigated. Composites were obtained with the thermal effusion of the polypropylene fusions with the CNT. Vibrational spectra were studied by the Raman scattering method, and the crystal structure of composites was investigated by the X-ray diffraction one.

With an increase in the fluence of electron irradiation (Å_å=1.8 MeV) both D and D* bands undergo noticeable changes, although the content of crystalline phase even with the small CNT concentration does not increase almost. This indicates the considerable increase in the density of phonon states near the boundary of Brillouin zone, which is reached due to the sp³ hybridization of polymer and CNT. At the same time the intermolecular seams are absent under the action of irradiation, although even with the large doses of absorption (3 MGy) the degradation of the composite components was not observed.

Phosphorescence of the ?-conjugated polymers with complex forming C₆₀ fullerenes during irradiation

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Film samples of the amorphous semiconductor polymers, which contain the ?- conjugated carbazole rings, in particular poly-N-vinylcarbazole (PVK) and poly-N-epoxypropylcarbazole (PEPK), are characterized by the migration of excitons on the singlet-triplet states. In this connection, the recombination of electron-hole pairs occurs upon T-S₀ transitions, that leads to the emission due to the triplet excitons. Since for the given polymeric samples, which widely are used for the conversions of solar energy, the space separation of charges after their photogeneration are important, then the significant role can play their sensitization by fullerene impurities. Furthermore, C_{60} molecules, that they absorb energy in the visible region, are capable to be the effective acceptors due to the high electron-affinity energy. In this case the creation of complexes with the transfer of charges and electron transport zones, which facilitate the appearance of significant distances of the thermalization of electrons, is possible.

In this work the samples, obtained with the simultaneous condensation of PVK or PEPK molecules and C_{60} fullerenes, were used. The molecules are evaporated on the silicon support from two sources at different temperatures of heating powders. C_{60} molecule concentration is changed with the speed of their evaporation. The thickness of the obtained films was about 100 nm. The irradiation of films was carried out by electrons with the energy of 1.8 MeV with the fluences.

With an increase in the content of C_{60} fullerenes the phosphorescence spectrum is displaced to the region of 732 nm, where the fluorescence of C_{60} fullerenes takes place. With an increase in the fluence of electron irradiation the phosphorescence spectra undergo noticeable changes, especially with the intermediate concentrations of C_{60} fullerenes. This indicates the growth of role of sp³ hybridization of electronic states in the "polymer–fullerene" system, that leads to the transformations of energy structure, because of which an increase in the effectiveness in the transfer of electrons and holes along the appropriate transport channels is observed.

Strongly non-linear carbon nanofibre influence on morphological and electrical properties of polymer composites

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Carbon nanofibres (CNF) are intensively studied during the last decade opening up new possibilities for tailor-made synthetic materials. The composite studied consists of CNF (diam. ca. 30–40 nm, length up 1 ?m) embedded into polymer matrix (styrene based latex) within a wide range of CNF concentration. A strong non-linear dependency of morphological, mechanical, and electrical properties was discovered.

The composites contained CNF (from 8 to 36 mass%), the latex mentioned above, surfactants, and aqua completing up to 100%. These composites were deposited on glass and fiber-glass plastic as a film coating or a single drop. The layer thickness (drop size) depends on liquid viscosity, which is controlled by aqua content. After removal of water solid coatings were obtained. Their conductivity, flexibility, and stability are significantly higher in comparison with pure latex. The latter is well known as a good insulator, however addition of CNF imparts it conductivity up to 100 mSm/cm. Layers of composite are more stable and durable, and no cracking was observed even for relatively thick layers (up to 1 mm).

Optical, mechanical, and electrical properties of coverings undergo a strong change (alike phase transition) in a particular narrow range of CNF concentration values. However, variations of CNF to surfactant ratio cause slight shift of that critical value. Anyway, the following effects are always well noticeable:

- The higher CNF concentration is, the less flexible and elastic the coverings are. At the critical concentration, coverings exhibit a rapid transition from an elastic rubber-like form to solid fragile layers. However, the adhesive properties remain almost intact.
- Analysis of optical images of coverings created shows a step-like raise of surface roughness when traversing the critical concentration range. Digital images were obtained, and their 2D derivatives were calculated with posterior averaging over the whole covering area. Both average absolute value of 2D derivative and its standard deviation exhibit an apparent raise (at 15–18% CNF loading), and then slowly decrease, thereby forming a local maximum. The same behaviour, with a local minimum is observed before the critical concentration.
- Electrical conductivity was measured using fibre-glass plastic substrates with copper planar contacts. Static impedance estimation was used along with precise volt-ampere characteristic measurements. Thus zero-voltage conductivity was calculated, which value exhibits a deep and sharp minimum corresponding to critical concentration. In this particular case, the volt-ampere dependency becomes temporarily unstable with numerous branches clearly distinguishable. Voltage increment causes the specimen to furcate between two or more stable states with particular conductivity level corresponding. The further raise of CNF loading is followed by conductivity decrease, hence a maximum is observed. Although the 100% CNF specimen is impossible to produce, it is very probable that conductivity enhancement is achieved.

Conductivity of the composite is almost invariable when changing the size of CNF particles. After milling pure CNF with average particle size decreased about ten times, conductivity changes did not exceed 7-10%. This may be an evidence of fractal structure of CNF globules which overall surface area remains almost intact after milling.

The obtained results reveal a strong structural transformation of composite layers when a particular CNF concentration is achieved. Quick and intensive change of different physical properties in a narrow range may correspond to transition between two competing paths of layer formation while drying; taking into consideration, that in liquid phase there is no analogous effect observed.

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Microwave and optical absorption of composite layers of carbon nanofibrs in dielectric polymer matrix

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Among plenty of applications of graphite, one is based on its high microwave radiation absorption capability. Taking into consideration the graphite-like structure of carbon nanofibres (CNF) it is expected to observe microwave absorption of materials containing CNF. One of the most effective ways to organise multiple discrete CNF globules into a relatively homogeneous layer without losing most of useful CNF properties is embedding them into polymer matrix. A mixture of fishbone and parallel type CNF was used, diam. 30–40 nm, length up to 1 ?m. Water-based composite contained a polymer latex with CNF (from 20 to 30 mass% in liquid state) and surfactants added. To perform measurements at higher frequencies up to IR, visible, and UV radiation a dilute compound was used: CNF concentration less than 1% and no surfactants added.

The surface morphology of composite layers depends primarily on two factors: average size of CNF particles and their concentration. It was shown [1], that concentration of CNF in latex strongly influences dried covering morphology in a significantly non-linear manner. The roughest surface was obtained considering that dependency. In order to preserve inner structure of CNF globules only moderate sonication was applied to homogenise the mixture. Liquid composite was deposited on glass (for microwave measurements) and quartz (for optical spectroscopy) and dried up. Thicknesses of layers were from 100 up to 250 ?m. Morphology of covering's surfaces was quite rough with typical size of surface irregularities 50 - 500 ?m; however, no coarse defects (such as cracks) were observed. Hence, such kind of surface ensures the lowest level of mirror reflection of microwave radiation. Moreover, the further investigation revealed that diffuse reflection is also immeasurably low.

Near field microwave transmission measurements were carried out according to the method described in [2] and using direct transmitter–detector scheme. Experimental results were analysed under the assumption of exponential fading of radiation intensity as the layer thickness rises. Considering glass substrate the film was deposited on, the following five parameters were calculated: absorption indices for composite and glass, and reflection coefficients on interfaces air–composite layer, composite layer–glass, and glass–air.

The calculated value of air-composite reflection level is less than estimated measurement error. Near field microwave radiation absorption was estimated, and its value with confidence exceeds 3.3 mm, hence 1 mm thick layer is capable of over 28 times reduction of radiation intensity. Since composite coverings produce very low reflection signal they may be used to suppress microwave impulse being echoed by metallic surfaces. This capability may be useful for individual protection purposes as well as other applications.

Optical absorption spectra were measured on layers produced of the dilute composite and compared with layers of pure latex. The relative spectrum (composite vs. latex) has apparent maximum and minimum conforming to energies 4.5 and 4.8 eV respectively. These values are close to work function of electron in graphite and may correspond to excitation of electrons in graphene sheets of CNF. If this suggestion is confirmed, the effect of light absorption on electrons may provide a possibility to estimate high frequency properties of CNF and composites based on them, hence leading to more precise modelling, computation, and measuring of both microwave and optical properties.

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Electrical properties of polypyrrhol composites polymerised in presence of carbon nanofibres

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During recent years, the number of publications dedicated to research of properties of polymer composites with carbon nanofibres (CNF) is increasing. However, most works investigate CNF embedded into preliminary polymerised substance, when the systems containing CNF in monomer prior to polymerisation are less studied. Our approach involves conductive polymer — polypyrrhol with CNF loaded before polymerisation. The synthesis was carried out according to [1] using mixture of parallel and fishbone type CNF, diam. 30–40 nm, length up to 1?m.

The solid substance obtained after polymerisation was dissolved in chloroform, which amount was chosen according to viscosity desired. The typical concentrations provide almost homogeneous coverings with thickness from 70 to 150 ?m depending on drying conditions. Application of subsequent layers over the first dried covering caused destruction of underlying film and formation of heterogeneous structure with multiple defects. The same effect was observed on glass, fibre-glass plastic and copper substrates.

Mechanical and adhesive properties of coverings are relatively low; the layers are fragile and may be easily damaged. Anyway, they are temporarily stable, do not spontaneously come off the substrate, and their electrical, optical and morphological properties can be measured without affecting layer integrity. Layer morphology depends mainly on the filler dispersity, i.e. the average size of CNF globules. In liquid state system stratifies quite rapidly, with the smallest CNF particles present in whole volume when the larger ones settle down. Thus, the smaller are the particles remaining in the liquid composite, the smoother layers are produced of it. However, electrical conductivity of the smoothest layers is the lowest.

Electrical properties of the coverings depend primarily on CNF contribution, with regard to the fact that pure CNF conductivity is more than thousand times higher in comparison with pure or moderately doped polypyrrhol. Thus, composite layers have an optimum value of CNF load as well as CNF dispersity. These optima provide both acceptable conductivity and relatively smooth surface. Incidentally, the latter is accompanied with better mechanical stability.

Particular attention was focused on measurements of volt-ampere characteristics of the composite films. The dependencies are apparently exponential with obvious growth of differential conductivity during voltage raise. The majority of specimens' exhibits from four to eight times augment of conductivity in high electric field (over 140 V/cm) relatively to extrapolated values at zero voltage. In spite of slow decrease of overall current during long-lasting application of electric field, the ratio of high to low field conductivities remains intact or even increases.

The specimens obtained using the liquid composite fraction with small-sized CNF particles had ohmic characteristic and very high resistance. This fact may be a significant clue to determine, whether the CNF globules are embedded into the polymer structure or are present as a mechanical mixture component. The dependence of conductivity on CNF particle size is a specific trait of systems with CNF embedded prior to polymerisation, in contrast to mechanical mixtures of preliminary polymerised substances with CNF, which are almost insensitive to particle size [2] due to fractal structure of a CNF globule [3].

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Structure and thermodynamic property investigations î f fullerene doped polystyrene films

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It was [1] early shown that there are different ways to dope polystyrene with fullerene. However, the polymer-fullerene composites structures were insufficiently studied and the information presents is mutually contradictious. It is noted, that on the one hand low fullerene concentration influence on composite properties is strong [2, 3], on the other hand the lack of the property change until concentration is less 1% mass [4].

The purposes of this paper are to produce polystyrene films modified with the low concentration fullerene mixture $(\tilde{N}_{60}+\tilde{N}_{7070})$, to investigate its structure and thermodynamic characteristics as well as the polymer interaction mechanism with nanocarbon particles.

The carbon black was obtained by the arc discharge method. Polystyrene modification was made by mixing fullerenes and polystyrene solutions in the same solvents (o-xylene). The film was obtained on the glass surface during solvent vaporization. The films obtained were studied using differential scanning calorimetry (DSC), IR and UV spectroscopy and X-ray analysis.

It was shown that fullerene mixture doping into the polystyrene leads to heat capacity increase and glass-transition temperature decrease. Various size and structure crystallite presence with interplanar spacings 2.3, 2.5 and 3.9A in fullerene doped films was detected using X-ray analysis method. It was suggested that the whole changes in IR and UV spectra caused Van-der-Waals complex of phenyl ring of the polymer molecule and fullerene.

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Aligned carbon multiwalled nanotubes - polymer composites

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Carbon polymeric nanocomposites (PNC) are of great interest for fundamental research and various applications. At present these new materials are being investigated extensively. Nanocomposites (films) are obtained in situ polymerization which involves polymer precursor comprising aligned carbon nanotubes. For this purpose it is necessary to obtain a stable homogeneous suspension of nanotubes with chosen concentration in liquid polymer precursor on the substrate surface placed in uniform electrostatic field. The post thermal treatment of suspension transforms it into a solid polymer composite. In work [1] we deduced the analytical condition to obtain stable ordered single walled nanotubes (SWNT) in polymeric materials: $E \ge \sqrt{4kT \ln |tgq|} / e_0 a / q$, here E is electric field strength, $?_0$ is electric constant, ? is the polarizabiluity, ? is the angle of nanotube rotation. The estimations under consideration require electric fields of the order of magnitude 10^5 V/cm. The values of polarizability of carbon multiwalled nanotubes (MWNT) presently unknown. In [2] the electronic properties of carbon nanotubes are investigated in strong electric fields. It is shown that nanotubes exhibit metalliclike screening of external electric fields. Electrons on the tube wall are polarized and electrons on the inner side of the tube are unaffected, which may be a general property of nanotubes. For this reason we used the magnitudes of static polarizabilities per unit length ?₁₇ of SWNT of various radius from [3] to estimate the value ? for MWNT. The characteristic radii and lengths of MWNT are over the ranges 2.5< R<15 nm, 1<L< 20 ?m respectively. For MWNT with R=5 nm and L=10?m by extrapolation data of [3] we obtained the value of polarizability ? = $?_{zz}L = 4.8 \cdot 10^8 A^{03}$. Therefore to align MWNT according to the above mentioned analytical condition the strength of the electrical fields is of one order of magnitude less than one in the case of SWNT.

To realize the method proposed we have developed a scheme and technique characteristics of the experimental device .

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Degradation mechanism of polymer chains in C₆₀ fullerene-polymer composites

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Nowadays, extensive studies of polymer nanocomposites are at the center of attention of polymer science. It was revealed that viscoelastic properties of nanocomposites change in comparison with these of pure polymers. It was shown that features of viscoelastic behavior of nanocomposites are manifested for polymers when its molecular weight (M) exceeds critical entanglement molecular weight M_e . Many researchers explain these features by limitation of chain mobility as a result of their interaction with nanoparticles. The ability of fullerene C_{60} to form molecular complex with polymers and solubility of C_{60} and its complexes give unique chance to study of polymer-fullerene composites in solutions.

The composites were prepared by lyophilization of mixed polymer and fullerene solutions. Composites of polystyrene, poly- α -methylstyrene, and polyvinylpyrrolidone were studied in solvents of different quality relative to C₆₀ using UV-spectroscopy and size exclusion chromatography. The dilution of composite (at polymer M>M_e) is accompanied by formation of covalent bound between polymer and fullerene confining chain degradation. Chain degradation is a random process; branched structures are formed as well as fragments of dimer and trimer dimensions. Degradation depends on M and concentration, the effect of zip length is observed. The obtained data are in agreement with the idea of consequences attending mechanical breakage of C-C-bond in chain backbone. Dependence of composite degradation on fullerene solubility in used solvents indicates that breakage of C-C-bond is caused by confined chain mobility due to existence of polymer-fullerene molecular complex. Degradation is not observed for polymers having M<M_e.

In that way by the example of polymer-fullerene composites it is shown that chain entanglement and confined mobility may lead to chain degradation. In the similar conditions chain degradation is also possible for other polymer nanocomposites.

Analysis of interactions in fullerene-solvent-polymer system by UV-spectroscopy

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It is well known that the unique feature of fullerenes is their rather good solubility in many organic solvents that allows using UV-spectroscopy for analyzing solutions containing fullerene. Potentialities of UV-spectroscopy for identification of interactions in fullerene-solvent-polymer system are used in this work.

Comparison of fullerene C_{60} spectra in different solvents (chloroform, tetrahydrofuran, benzene, toluene, and paraxylene) indicates different mechanisms of fullerene dilution. It is found that the existence of critical concentration of C_{60} in benzene and toluene results in spasmodic change of fullerene spectrum at this value. Probably, in this case the abrupt change is caused by the onset of fullerene aggregation in solutions.

In solutions absorption of fullerene vastly exceeds that of a polymer; that allows us to treat polymer-fullerene interactions according to changes of fullerene UV-spectrum. It is shown that in fixed solvents spasmodic change of C_{60} spectrum takes place on reaching chain entanglement concentrations in mixed solutions of polymer and fullerene. Probably, this fact indicates chain unfolding and onset of chain-fullerene interaction. UV-spectroscopy makes it possible to identify the formation of polymer-fullerene molecular complex. By the example of 2- and 6-armed star polymers with fullerene C_{60} as the branchpoint, the possibility of identification of covalent bond between polymer and fullerene is demonstrated.

Membranes based on star $\tilde{N}_{60}\mbox{-}containing polystyrenes for effective gas separation$

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Special synthesis of polymers with high structural organization is a promising trend in devising new materials for membrane technology. Star polystyrenes with fullerene C_{60} as a branching center exhibit highly symmetric structure and very low polydispersity in molecular weight distribution. Due to the peculiarities of polymer chemical structure and the fullerene C_{60} presence, these materials demonstrate specific physical properties, including the ability to form films with highly ordered structure ("honeycomb morphology"), which is very promising for the formation of separating membranes.

Synthesis of star polymers with regulated architecture is based on anionic polymerization technique [1]. Regular star polystyrenes with fullerene C_{60} core, which exhibit molecular weight of each arm equal to $120?10^3$ g/mol and number of arms equal to 6, $C_{60}(PS)_6$, or 12, $(PS)_6C_{60}$ - $C_{60}(PS)_6$, were synthesized. These polymers were dissolved in chloroform and used for preparation of homogeneous membranes by solvent evaporation on cellophane surface at 30° N. Gas transport properties were studied by use of standard mass-spectrometry method for measuring permeability of H₂, He, N₂, O₂, CO, CO₂, and CH₄. Transport of small molecules is a method that is sensitive to change of polymer density. Density of homogeneous membranes with thickness 120 µm was determined by a flotation method in a saccharose solution at 25°C.

Membranes based on star polystyrenes exhibit excellent gas transport properties. Permeability coefficients of all gases for $(PS)_6C_{60}$ - $C_{60}(PS)_6$ are lower than that for $C_{60}(PS)_6$. The reason is enhanced density of $(PS)_6C_{60}$ - $C_{60}(PS)_6$ that leads to decreasing polymer free volume and gas permeability. It should be noted that CO permeability coefficient for both $C_{60}(PS)_6$ and $(PS)_6C_{60}$ - $C_{60}(PS)_6$ is anomalously high. To determine the position of membranes from star polystyrenes among known polymer membranes, Robeson's diagram was used. This diagram characterizes dependence of \tilde{NI} / N_2 selectivity on CO permeability of all known membranes. On Robeson's diagram the data of our membranes is located higher than "upper bound" line, that is, gas separation properties of $C_{60}(PS)_6$ and $(PS)_6C_{60}$ - $C_{60}(PS)_6$ for \tilde{NI} / N_2 mixture are better than these of known membranes.

Thus, membranes based on $C_{60}(PS)_6$ and $(PS)_6C_{60}-C_{60}(PS)_6$ can find effective application for \tilde{NI} /N₂ separation in synthesis-gas production.

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Structure and hydrodynamical properties of heteroarm C₆₀ fullerene-containing polymers

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Star-shaped polymers with fullerene C_{60} as branching center and polystyrene and poly-(2-vinylpyridine) arms were synthesized using anionic polymerization techniques; the conditions of modification of macroinitiator (hexaadduct of polystyryllithium with fullerene C_{60}) were varied. Translational diffusion and viscometry in benzene solutions were used to determine molecular masses, hydrodynamical radii and functionality of heteroarm molecules. Hydrodynamical data were compared with the properties of linear analogues and interpreted using the model of regular star. It was shown that during the formation of heteroarm macromolecules with controlled number and molecular masses of arms the determining stage is the process of modification of hexaadduct with 1.1-diphenylethylene. If the synthesis is performed under the conditions when the elimination of "living' polystyrene chains from hexaadduct-precursor is possible, heteroarm polymers with, on average, four arms of polystyrene and four arms of poly-(2-vinylpyridine). When the synthesis is performed under optimized conditions in non-polar meduim, we obtain star-shaped molecules with total number of arms close to 12, which corresponds to the defined structure, containing six arms of polystyrene and six arms of poly-(2-vinylpyridine).

Properties of star-shaped polymers with fullerene core in solutions

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Regular poly(styrene) stars $(PS)_6C_{60}$ having single center and doublecentered stars $(PS)_6C_{60}$ -[Si- $(CH_3)_2$]-C₆₀(PS)₆ were studied in different solvents using static and dynamic light scattering, and viscometry as well. The molecular mass of arm (M_{arm}) was varied from $4 \cdot 10^3$ up to $120 \cdot 10^3$.

The obtained values of intrinsic viscosity for all the samples studied are compared with theoretical values calculated for star-shaped macromolecules with definite number of arms. It is observed that both $(PS)_6C_{60}$ and $(PS)_6C_{60}$ -[Si- $(CH_3)_2$]- $C_{60}(PS)_6$ by their hydrodynamic properties correspond to the model of star-shaped polymeric coils with strong hydrodynamic interaction between segments. Moreover, the ratio of R_g/R_h (R_g , R_h are the radii of gyration and the hydrodynamic radii, accordingly) obtained from light scattering experiments is 1.4 which is typical for star-like polymers.

Properties of poly(styrene) stars were compared with linear $(PS)C_{60}$ macromolecules where fullerenes are located on the ends of chains.

Self-assembly of fullerene molecules in thin polymer films. Some practical applications

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Last years much attention has been paid to the use of fullerenes for the development of the new generation of polymer materials. Strictly speaking, fullerenes are not nanostructured materials, but the specific features of their molecular structure provide however wide prospects in nowadays polymer material science. The work comprises a comparative study on the structure of fullerene suspensions in order to obtain the preliminary data for the characterization of fullerenes as physical modifiers of polymer matrix. Fullerene \tilde{N}_{60} synthesized by us was used in the study. The processes of fullerene self-assembly in the solvent medium and the influence of various factors (such as, the change of concentration, time and ultrasound field intensity) on this process have been studied by dynamic light scattering and electron microscopy.

It was shown by electronic microscopy that under correctly chosen conditions of sonication it is possible to prepare fullerene clusters with the average diameter of 50 nm. Self-assembly process and sedimentation resistance of fullerenes in polymer liquids have been studied. High ability of fullerene for self-dispersion in polymer matrix has been shown that allowed us for the first time to obtain stable fullerene nanoclusters. As a result, the fullerene-containing thin films were prepared. They show the same photodynamic properties as fullerene itself promoting the conversion of triplet oxygen to its highly active singlet form.

Charge-separation effect on dielectric and electrooptical properties of 6-arm polystyrene stars with fullerene core in solutions

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The molecular properties of fullerene-containing polymers depend on the carbon nanoparticle-macromolecule chemical linkage type and on fullerene's state inside of polymer coil [1, 2]. In the case of star-like covalent type fullerene derivatives of highly symmetric structure (similar to T_h) it was predicted a possibility to observe a strong charge-separation effect connected with electrons transfer between addend-donors and 3-dimentional fullerene-acceptor [3]. At the present work two samples of 6-arm polystyrene (PS) stars $A_6C_{60}(PS)_6$ with the variation of low molecular addends, A (Fig.1), have been studied in benzene solution by the methods of electrooptical Kerr effect (pulsed electric fields) and dielectric polarization (radio frequency electric fields).



Figure 1. Structure of $A_6C_{60}(PS)_6$; molecular mass of PS-arm was $4x10^3$.

It was detected that specific dielectric polarization and electrooptical characteristics of $A_6C_{60}(PS)_6$ are in order of magnitude higher than that of fullerene free PS-macromolecules of the same molecular mass. Experimental results were explained by the effect of long-live (?s) charge-separation states of S₆-symmetric core (C₆₀ adduct) at the centre of polymeric stars. It was also shown that the difference in molecular properties of samples under investigation is not significant, but the displacement of addends A=–H by A=–CD₃ evidently leads to increasing of dielectric and electrooptical characteristics of A₆C₆₀(PS)₆.

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[60]Fullerene-containing liquid-crystalline codendrimers: synthesis, characterisation and applications

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Materials consisting of dendritic macromolecules decorated by special functional groups are multifunctional compounds that may be used for the design of Langmuir-Blodgett films and self-organized monolayers. Fullerene-containing liquid-crystalline dendrimers belong to such supramolecular materials. Interestingly, they combine the properties of liquid crystals (LC) with the photo- and/or electrochemical properties of fullerenes. Therefore, they may be used as photosensitive materials [1].

Two approaches have been developed for the design of [60]fullerenecontaining thermotropic LCs [2]. The latter were synthesized via either the Bingel-addition reaction or the 1,3-dipolar cycloaddition reaction, leading to methanofullerenes [2, 3] and fulleropyrrolidines [2, 4], respectively. Nematic, smectic A, smectic B and columnar phases were observed for these compounds. Recently, we were able to synthesize fullero(codendrimers). In this case, the liquid-crystalline properties can be controlled more precisely as the size of each dendron can be adjusted by synthesis (synthetic modular approach).

We will present the main features for the synthesis of [60]fullerenecontaining LC dendrimers and codendrimers and the molecular properties of these compounds in solution (size, shape, permanent dipole moments, specific dielectric polarization, and electrooptical properties). Particular attention will be devoted to the "structure-properties" relationships. It will be demonstrated that the structure of the dendrons [poly(aryl ester) dendron or poly(benzyl ether) dendron] and their generation number play a crucial role in the formation and structure of the mesophases. Possible applications of those materials based on cylic voltammetry experiments and electronic properties will be discussed.

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