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# Assessing carbon nanotube arrangement in polystyrene matrix by magnetic susceptibility measurements



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# ABSTRACT

Multi-wall carbon nanotubes filled with iron nanoparticles were combined with polystyrene to evaluate interface interactions and nanotube orientation in composite using magnetic susceptibility measurements. Iron-containing species were introduced into MWCNT cavities as the result of catalytic chemical vapor deposition synthesis using ferrocene as a catalyst source. Polystyrene loaded with certain quantity of MWCNTs was uniaxially stretched to provide the nanotube alignment. Magnetic susceptibility measurements performed in three perpendicular directions of magnetic field confirmed the alignment in the stretching direction. The composites showed a large diamagnetic response in a magnetic field perpendicular to the nanotube axis and low response in a parallel field. In a quantitative sense, anisotropy exceeds by more than an order of magnitude the effect expected from intrinsic susceptibility of nano-tubes. Apparently, the graphitic nature of the nanotube lattice results in strong non-covalent interactions with uniaxially stretched polymer matrix, and aromatic rings as side groups of polystyrene align parallel to the nanotube surface, contributing to strong diamagnetism. As magnetic susceptibility is a penetrative but non-destructive type of measurement, it can successfully characterize both the alignment of one-dimensional or two-dimensional carbon allotropies and the arrangement of the macromolecules around them, contributing to the optimal design and performance of nanocomposites.

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# 1. Introduction

The composites of carbon nanotubes (CNTs) with organic matrices hold out promices for improved electrical, thermal and mechanical properties. The polymers with aligned nanotubes are considered to be particularly promising materials for many anisotropic applications including heat sinks [1], data storage [2] and cost-effective and lightweight EMI shielding [3]. It was shown that the higher the orientation, the higher the polymer composites' mechanical strength and shielding effectiveness. Moreover,

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orientation of CNTs in matrix resulted in an anisotropic response of polymer composite relative to low-frequency [4] and terahertz radiation [5]. The composites were significantly transmitted in out-of-plane direction due to much higher polarizability of a CNT along the axis. Another important issue is the amount of CNTs in the matrix: the application of nanocomposites can be practical once the weight percentage of CNTs and, in turn, cost is minimized.

Whereas different methods for obtaining aligned CNT composites have been advanced [6], the characterization of alignment of both nanotubes and macromolecules is a complicated task. Noncrystallinity of the materials, elemental identity of the filler and the matrix hinder the application of diffraction and spectroscopic methods, whereas transmission electron microscopy (TEM) and atomic force microscopy (AFM) provide only local and surface assessment. Also, the final composite properties are influenced by



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the dispersibility of nanotubes. Not all methods which are traditional for the charaterization of CNTs can be used for the CNT-based composites due to a low content of the filler and masking or interfering effect of matrix. This requires a comprehensive search of alternative approaches for the evaluation of the structural characteristics of composites. Recently, we have shown that aspect ratio and alignment of CNTs in a polymer can be determined by modeling the frequency dependence of electromagnetic response using a modified Clausius-Mossotti model [7].

In this work we demonstrate that measurements of magnetic susceptibility provide valuable information about the orientation of both carbon nanotubes and the polystyrene macromolecules. MWCNT/polystyrene composite is regarded as a three-component magnetic system, where the iron-based nanoparticles elongated in the nanotube cavity act as anisotropic magnetic species allowing the evaluation of CNT orientation in a composite film. Analysis of anisotropic diamagnetic susceptibility unambiguously manifests wrapping of polymer chains around the aligned MWCNTs. Studies of the composites with 1, 2.5 and 5 wt% of MWCNTs in polystyrene matrix revealed that the best alignment is achieved for the smallest nanotube concentration.

# 2. Samples

# 2.1. Synthesis

MWCNTs were produced using aerosol-assisted catalytic chemical vapor deposition (CCVD) method. The synthesis was carried out in a horizontal tubular reactor, which was described in detail previously [8]. Silicon substrates with a size of  $10 \times 10 \text{ mm}^2$  were located in the central part of the reactor, then the reactor was pumped, filled with argon gas and heated up to 800 °C. Ferrocene (2 wt%) was dissolved in toluene and the reaction mixture was injected into the reactor with a rate of 0.14 ml/min. The pyrolysis was performed at atmospheric pressure in an argon flow (250 cm<sup>3</sup>/min) for an hour. Examination of product by scanning electron

microscopy (SEM) on a Hitachi S-3400N microscope revealed covering of silicon substrate by MWCNT array (Fig. 1(a)). In the array, nanotubes are well aligned and oriented normally to the substrate surface. Cleavage of the sample for SEM study resulted in a gap between array and substrate. This is indicative of weak interaction of the constituents, which allowed to separate the CNTs easily. For TEM investigation, the CNTs were mixed with ethanol and after ultrasonication the suspension was deposited on colloidal carbon film grid. TEM images obtained on a Jeol JEM 2010 microscope showed that CNTs are multiwall with an interior cavity of ~10 nm (Fig. 1)(b) and (c). Dark-contrast nanoparticles observed on the TEM images correspond to metallic compounds produced from ferrocene Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>. Mössbauer spectroscopy study of CNTs synthesized by the same method detected three forms of iron nanoparticles, namely, two magnetic phases α-Fe and Fe<sub>3</sub>C and one nonmagnetic  $\gamma$ -Fe phase [9]. From the results obtained after the MWCNT treatment with a diluted sulfuric acid, it was supposed that the  $\alpha$ -Fe phase is mainly located close to the CNT ends, while the  $\gamma$ -Fe and Fe<sub>3</sub>C phases are inside of the channels [10]. TEM images presented in Fig. 1(b) and (c) show that the iron nanoparticles are elongated while part of them have a near spherical shape.

#### 2.2. Composite preparation

Polystyrene plates with 1, 2.5, 5 wt% of multi-wall carbon nanotubes (MWCNTs) loading were prepared using the stretching method [11]. A required amount of CNTs separated from the silicon substrate was put into a toluene solution of polystyrene and the mixture was mechanically stirred until complete polymer dissolving. Then, the suspension was sonicated for ~2 min using a high-power sonic tip (200 W) with the purpose to improve the MWCNT dispersion. Freshly produced slush was cast onto metallic substrate and dried to a viscous state at ambient conditions. A soft composite plate was uniaxially stretched at a constant speed of 0.2 mm/min under heating (~70 °C), which was provided by a hot air gun. A microscrew setup led to an increase of the axial plate size



**Fig. 1.** SEM images of aligned MWCNT array vertically grown on Si substrate (a), low-resolution (b) and high-resolution (c) TEM images of MWCNTs from the array. (d) AFM image of the MWCNT-polystyrene composite. To assess variable structural regions, the 3D topography with the phase channel were superimposed. Arrows show the location of the MWCNTs embedded in polystyrene. (A color version of this figure can be viewed online)

up to 100%. Finally, the composites were dried under a light load at room temperature. All the prepared plates had visually homogeneous grey color. Fig. 1(d) represents the results of the AFM Semicontact Tapping mode with the phase channel overlaid on 3D topography of the stretched sample containing 5% MWCNTs. In AFM topography image the nanotubes are hardly visible because they are coated with polystyrene, but they are easily detectable in the phase image due to the difference in Young's moduli. The MWCNT are located in the film plane and are mostly oriented in the stretching direction. We have verified that their orientation persists over the samples on larger 20  $\mu$ m scan images for all samples. Investigation of the electromagnetic response of the composites prepared by the above described techniques detected that the nanotubes indeed have a predominant orientation in the film planes [4,5,7].

## 3. Experimental results

#### 3.1. Polystyrene

Firstly, we examined stretched unfilled polystyrene films, prepared using the technology described above. Magnetic measurements were performed in three configurations, magnetic field was: (1) perpendicular to the film surface ( $H_{\perp}$ ), (2) parallel to stretching direction ( $H_{II}$ ), and (3) in-plane but directed perpendicular to the stretching ( $H_{\perp II}$ ). In further description we will mainly compare results for  $H_{\perp}$  and  $H_{II}$ , paying attention to  $H_{\perp II}$  when necessary.

Thermomagnetic measurements at 2–400 K as well as the measurements of isothermal field dependencies of magnetization taken at 3, 100 and 300 K revealed a temperature-independent diamagnetism of stretched polystyrene in the interval of 50–300 K. Below 50 K, a Curie paramagnetism was observed from which the concentration of unpaired spins was determined. The most striking result is that diamagnetism of the stretched film is strongly anisotropic. Fig. 2(a) shows room-temperature M(H) dependencies for two orientations of magnetic field; magnetic susseptibility  $\chi$  is calculated from the slope of these curves. The difference  $\Delta \chi = \chi_{\rm II} - \chi_{\perp}$  equals to  $0.8 \cdot 10^{-6}$  emu/g Oe in the studied temperature range.

One can estimate the theoretical value of diamagnetism for the styrene molecule using the Pascal constants:  $\chi = -0.53 \cdot 10^{-6}$  emu/g Oe. This value is very close to the measured  $\chi_{\perp}$  value for stretched polystyrene:  $\chi_{\perp} = -0.6 \cdot 10^{-6}$ . By contrast, the absolute value of  $\chi_{II}$  is significantly greater:  $\chi_{II} = -1.4 \cdot 10^{-6}$ . The measured effect for  $\chi_{II}$  correlates well with the fact that a considerable increase in the diamagnetic susceptibility and high anisotropy are typical for delocalized cyclic compounds. Polystyrene contains phenyl rings, and value for the anisotropy of the diamagnetic susceptibility for the rings equals to  $-1.11 \cdot 10^{-28}$  emu/molecule [12], which yields  $\Delta \chi = -0.86 \cdot 10^{-6}$  emu/g Oe, very close to the measured  $\Delta \chi$  value.

The stretching procedure could orient the aromatic rings inplane (Fig. 2, model 1a) or out-of-plane (Fig. 2, model 1b) to the film. As  $\chi_{II} > \chi_{\perp}$ , the polymer axis is aligned along the stretching direction whereas the aromatic rings are perpendicular to it. The comparison of measurements at the field directions H<sub>II</sub>, and H<sub> $\perp$ II</sub> shows that a misalignment of the rings is approximately 20% supporting the model 1b. Our results indicate that benzenes favor structures in which the aromatic rings are parallel.

In our experiments, polystyrene films were stretched up to 30% and 100% of initial length. The difference between  $\chi_{\perp}$  and  $\chi_{II}$  is the same for both films:  $0.8\cdot 10^{-6}$  emu/g Oe. The only distinction which was revealed in magnetic measurements is the localized spin concentration due to the dangling bonds: for the 30% stretched film  $N_s=4.3\cdot 10^{18}~g^{-1}$ , for the 100% stretched film  $N_s=1.6\cdot 10^{19}~g^{-1}$ . Therefore, excessive stretching does not improve the structure by orientational effect, but breaks more bonds.

#### 3.2. MWCNTs on silicon

Next, we made magnetic characterization of the nanotube forest. Total magnetic response of the MWCNTs on silicon substrate is dominated by the nanoparticles from iron-based catalyst which constitutes 3% of MWCNTs weight. Fig. 3(a) shows hysteresis loops for the in-plane direction (perpendicular to the tube's axis) and out-of-plane (parallel to the tube's axis), respectively. A clear uniaxial magnetic anisotropy is seen, with an easy axis parallel to the MWCNT axis.

It is possible to obtain intrinsic magnetic susceptibility of MWCNTs from a linear slope of the magnetization curve in the region 2–5 T, because magnetization of the ferromagnetic nanoparticles saturates above 2 T. The magnetism of carbon nanotubes is determined by orbital diamagnetic susceptibility which is strongly anisotropic: it shows a large diamagnetic response in a magnetic field perpendicular to the tube axis. From both theoretical [13] and experimental findings, orbital diamagnetism of a CNT strongly depends on the diameter. In case of SWCNTs the difference  $\Delta \chi$  is in the range from -1 to  $-3 \cdot 10^{-6}$  emu/g Oe for the nanotubes with 1–3 nm diameter [14]. In our case, the outer diameter of MWCNTs is 15–20 nm, and the anisotropy value should be closer to that of graphite. The fitting parameters from the M – T curves yield  $\Delta \chi = -10 \cdot 10^{-6}$  which seems reasonable.

The behaviour of metallic nanoparticles encapsulated into inner CNT channels has been a subject of extensive studies, which emphasised that indirect exchange coupling between magnetic nanoparticles in CNT matrix could influence magnetic properties of the entire system [15,16]. Fig. 3(a) shows isothermal M(H) dependence with typical features of superparamagnetic behaviour of an ensemble of partially oriented magnetic nanoparticles. The obtained coercivities are larger than those reported for bulk Fe<sub>3</sub>C. In superparamagnetic particles, the magnetization reversal occurs via



Fig. 2. (a) Field dependence of magnetization for a stretched unfilled polystyrene film. (b) Possible structural models accounting for strong difference in diamagnetic susceptibility for the magnetic field directed parallel and perpendicular to the film surface.



**Fig. 3.** (a) Field dependence of the magnetization for the MWCNT on silicon substrate at T = 3 K and at different orientations of the sample versus magnetic field. (b) Coercivity variations with temperature (2 < K < 300). Magnetic field is parallel to the nanotube axis (open symbols) and perpendicular to it (closed symbols).

the rotation of the magnetization vector from one magnetic easy axis to another one via a magnetically hard direction. As a consequence of this rotation mechanism, the coercivities of magnetic nanoparticles differ from those of bulk counterparts. It was shown by both simulations and experimental measurements that ferromagnetic nanowires with the Fe<sub>3</sub>C crystal structure reveal large coercive fields which strongly depend on the magnetic particle diameter but are not affected by the length of the particles [17].

Hysteresis loops indicate smaller coercive field for in-plane field orientation compared to that for out-of-plane orientation. At 2 K the in-plane coercivity ( $H_{CII}$ ) is 1400 Oe whereas the out-of-plane coercivity ( $H_{CL}$ ) is 1100 Oe. This is the consequence of alignment of the magnetic particles inside aligned nanotubes: in the case of an elongated nanoparticle it is easier to magnetize along a long axis because demagnetizing field is smaller in the long direction.

Temperature dependence of coercive force for both directions is plotted in Fig. 3(a). Decrease of the coercivity due to the thermal fluctuations is described by Sharrock equation:

$$H_{C}/H_{0} = 1 - (25 k_{B}T/KV)^{n}$$
(1)

where H<sub>c</sub> is the remnant coercive field, the constant K is the effective magnetic anisotropy, approximately given by  $K = 25 k_B T_B/$ V, T<sub>B</sub> being the blocking temperature and V is the nanoparticle volume, k<sub>B</sub> is the Boltsman constant. The exponent n is related to the orientation of the anisotropy axis. The frequently used value n = 0.5 is appropriate only for the coherent reversal case for a system with identical easy axis angles [18]. Sharrock law behavior also occurs with n ~0.67 for a distribution of easy axis [19]. In addition, in random assemblies not only irreversible (switching) processes, but also reversible (rotational) processes determine the magnetization curve. Since only switching processes are thermally activated, therefore the temperature decrease of H is even slower and the value n=0.77 was suggested [20,21]. In Fig. 3(a) we show the dependence of the coercivity  $H_C$  on  $T^{0.77}$  values of the temperature for the parallel and perpendicular orientations. Their linear dependencies confirm that the magnetic moments of ferromagnetic particles are aligned along their anisotropy axis supporting the disordered state [22].

### 3.3. MWCNT-polystyrene composites

We start the description of magnetic properties of MWCNTpolystyrene composites with comparison of magnetic properties of iron nanoparticles in the MWCNT-polystyrene matrix with those in the naked nanotubes.

Isothermal magnetization measurements were performed in two different configurations, namely magnetic field with respect to the film was directed in-plane and out-of-plane (Fig. 4(a)). We used the ZFC (zero field cooling) and FC (field cooled) measurements protocols (Fig. 4(b)). For the ZFC experiments, the samples were cooled from above room temperature to 2 K in the absence of magnetic field; thus, the nanoparticle moments were blocked along the anisotropy directions. The magnetic moment of each nanoparticle was lying along the magnetic easy axis being energetically degenerate with respect of the parallel and antiparallel direction. Then a small magnetic field was applied and magnetization was recorded upon heating. The increase of temperature overcomes the anisotropy energy thus releasing the moments and aligning them in the field direction. This process led to the increase of the magnetic moment. When the field was applied parallel to the film surface, the measured moment increased up to the temperature 340 K defining the superparamagnetic average blocking temperature  $T_B$  for the nanoparticle assembly. Above  $T_B$  the nanoparticles overcome the energy barrier and jump freely between the parallel and antiparallel directions, thus the moment decreases. In FC measurements, the samples were cooled at the presence of magnetic field. At  $T > T_B$  the thermal energy randomizes the magnetic moment, and on cooling the moments become aligned along the field direction leading to the increase in magnetization down to the lowest temperature of the experiment. From the  $T_B = 340$  K (maximum at the ZFC curve) we can estimate the average particle volume as 1000 nm<sup>3</sup> which matches well the linear dimensions obtained from TEM pictures (Fig. 1).

For the out-of-plane measurements, the superparamagnetic behaviour was not observed. As the magnetic easy axis is parallel to the long axis of the nanotubes, magnetic moment prefers to point along the nanotubes. Therefore, the strong qualitative difference between in-plane and out-of-plane magnetic measurements indicated that the MWCNTs are aligned in the film plane. We note that below 20 K the field dependencies of magnetic moment are affected by two factors: (i) an upturn due to Curie paramagnetism from intrinsic defects and (ii) some aligned MWNT arrays reported previously exhibited diamagnetism due to superconductivity [23]. Therefore, measurements at higher temperatures are more reliable for accessing nanotube arrangement.

Another interesting feature of MWCNT-polystyrene matrix is the enhanced coercive force compared to naked nanotubes. The variation of the coercivity with temperature is shown in Fig. 4(c) for both the parallel and the perpendicular field orientations. For both directions, there is surprisingly high difference of approximately 40% between the coercive force of the embedded and naked nanotubes.



Fig. 4. (a) The model of MWCNT arrangement inside polystyrene film. (b) ZFC-FC measurements of magnetic susceptibility of MWCNT-polystyrene matrix. (c) Coercivity variations with temperature (2 < K < 300) for MWCNTs and MWCNT-polystyrene matrix. Magnetic field is parallel to the film plane (open symbols) and perpendicular to it (closed symbols).

H<sub>c</sub> is highly susceptible to the anisotropy of nanoparticles, including shape anisotropy, surface anisotropy, stress anisotropy, and unidirectional anisotropy. As the geometric parameters of the nanoparticles are the same, and the preference for spins to align in a particular direction changes in consequence of coating the nanotubes with styrene, one should consider surface (interface) anisotropy. This effect should be attributed to the exchange interaction between the ferromagnetic core of the nanoparticle and the antiferromagnetic carbon shell. This interaction has the effect of the enhanced interface anisotropy which causes a considerable increase in the coercive field of the nanoparticles. The increase of coercivity in the composite may arise due to creation of pinning centers for the core moments during demagnetization [24]. Therefore, magnetic measurements revealed that the interactions between iron carbide nanoparticles and organic shells provide a source for additional anisotropy.

The magnetic susceptibility of the MWCNT-polystyrene composites was measured for three MWCNT concentrations: 1%, 2.5% and 5%. Measurements were done in the range 2–300 K, while Fig. 5(a)–(c) represent the room temperature results. Main panels show the linear magnetic response obtained after subtracting the nonlinear contribution from the catalyst nanoparticles, whereas the as-measured M(H) dependencies are shown in the insets of Fig. 5(a)–(c).

As in the case of pure polystyrene films (Fig. 2), strong anisotropy of diamagnetic response is observed for all MWCNT concentrations. In the simplest scenario, one could expect that the nanotubes are aligned between the polystyrene chains (Fig. 5(e), model 2a). In this case, the diamagnetic response will be only slightly modified due to the very low concentration of the nanotubes. Indeed, when we use a polystyrene matrix with  $\Delta \chi = 0.8 \cdot 10^{-6}$  emu/g Oe and add 1% of carbon nanotubes with  $\Delta \chi = -10 \cdot 10^{-6}$  emu/g Oe in the reversed direction, then in the frames of model 2a we can expect that the anisotropy will decrease by  $0.1 \cdot 10^{-6}$  emu/g Oe. In the experiment we observe radical changes in the magnetic behaviour: the anisotropy increases and changes its sign. When the field is applied in perpendicular direction, diamagnetism becomes stronger than in parallel (Fig. 5(d)). The only plausible explanation is the re-orientation of aromatic rings and wrapping the nanotubes as shown in Fig. 5(e), model 2b.



**Fig. 5.** Linear part of room-temperature magnetic response of MWCNT-polystyrene composites at different MWCNT filling: 1% (a); 2.5% (b); 5% (c). Insets in (a)–(c) represent the asmeasured data, magnetic field is parallel to the nanotube axis (open symbols) and perpendicular to it (closed symbols). (d) Difference between parallel and perpendicular magnetic susceptibility ( $\Delta\chi$ ) as a function of MWCNT content in polystyrene composite. (e) Models for different mutual arrangement of MWCNTs and polystyrene macromolecules.

The decrease of the effect with increasing the MWCNT content (Fig. 5(d)) is probably related to the nanotube agglomeration on the preparation stage.

## 4. Discussion

The results of magnetic measurements have revealed that in uniaxially stretched polystyrene films the aromatic phenyl rings are oriented perpendicular to the stretching direction whereas in MWCNT-polystyrene composites the rings follow the nanotube planes. Orientation of macromolecules in the presence of carbon nanotubes was previously reported for several nanocomposites, e.g. polyethylene and nylon [25]. From the comparison of CNT-epoxy and CNT-polymethylmethacrylate composites it was concluded that the molecular structure of polymer matrices, in particular the presence of aromatic rings, has a substantial influence on its binding affinity with CNTs [26]. Addition of MWCNTs has an hindrance effect on the preferred orientation of the syndiotactic polystyrene molecules [27]. Carbon nanotubes at very low concentrations act as nucleating agents for isotactic polypropylene (iPP) where the iPP macromolecules are wrapped around rather than aligned along the CNTs. Similarly to our results, this effect is more noticeable at the lower filler content analyzed, where it was proposed that orientation of the very first molecules, probably adsorbed at the surface of the MWCNTs, induces the formation of a stable structure [28].

An important point for understanding the magnetic results is aromaticity of the polymer matrix. Molecular dynamic simulations on two aromatic polymers, polyphenylene sulfide and polystyrene showed that the orientation of polymer chains is crucial for the interfacial interaction for both systems: by forcing the polymer chains expanded along the surface of the nanotube, the coating effect is strongly improved [29]. The driving force of the coating effects are the aromatic interactions which represent one of the principal non-covalent forces governing supramolecular organization and recognition processes.

Realization of strong interactions between the carbon nanotubes and polymer matrix is one of the topical issues in composite research. The polymers containing aromatic rings are the most attractive in this respect, and the stretching orientation was shown to be a highly efficacious pathway to achieve interfacial enhancement in polystyrene [30] The extraordinary reinforcement of CNTpolystyrene composite systems with highly oriented structure was reported [31,32], whereas for the non-oriented matrices this effect was weak [33]. Here we demonstrate the naturally emerging stacking between benzene rings and graphite hexagonal carbon and show that strong interaction between polystyrene resin and CNTs occurs in the situation of structural orientation. Samples with strongly anisotropic diamagnetic properties should be promising for designing high-performance polystyrene/CNTs composites.

## 5. Conclusions

Measurements of magnetic susceptibility and isothermal magnetisation loops were employed to assess the orientation of carbon nanotubes in polystyrene matrix as well as the orientation of polystyrene macromolecules. Uniaxial stretching of polystyrene films using the procedure described above leads to the alignment of both nanotubes and the polystyrene macromolecules.

The arrangement of nanotubes was evaluated on the basis of superparamagnetic behaviour of elongated iron-based catalyst nanoparticles in the inner cavities of MWCNTs. We found that the coercive force related to superparamagnetic nanoparticles of the Fe<sub>3</sub>C catalyst inside the MWCNTs embedded in polystyrene matrix is strongly enhanced compared to the same nanotubes but without

polystyrene. This is a direct experimental confirmation for the predictions about the existence of exchange coupling between magnetic atoms and carbon matrix [34]. The arrangement of the stretched composite films exhibit very strong anisotropy of diamagnetic susceptibility. The difference of linear magnetic susceptibility in the direction of uniaxial stress and perpendicular to that exceeds by more than an order of magnitude the effect which could be brought by the nanotubes alone. Carbon nanotubes have a graphitic lattice, thus they can act as templates for sticking of the polystyrene macromolecules containing aromatic rings with consequent non-covalent wrapping. As a result, the phenyl rings become oriented perpendicular to the stretching direction which is detected by anisotropy of magnetic susceptibility. Magnetic measurements of nanocarbon-based polymer composites offer a new source of information on their structures.

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