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1 Introduction

In the recent decade the liquid crystal (LC) suspensions of carbon nanotubes (CNTs) have attracted great interest (for a review, see ref. 1–6). These hybrid systems represent mixtures of molecular and nano-sized anisotropic species with a range of new opportunities for each of these components. On the one hand, the LC phase imposes orientational order to CNTs. Moreover, the LC driven self-assembly of CNTs can be tuned by external electric or magnetic fields.^{7–9} On the other hand, CNTs bring many intriguing properties to LCs so that the LC + CNT composites are unique metamaterials with promising applications in electrical engineering, optics, optoelectronics and nanoscience. In particular, doping of LC by CNTs can essentially improve the electro-optic performance of LC cells,⁶ induce electro-optical^{1,10,11} and electromechanical¹² memory effects and enhance permittivity and electrical conductivity^{13,14} in these systems.

Structural evolution and dielectric properties of suspensions of carbon nanotubes in nematic liquid crystals[†]

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Structuring of carbon nanotubes (CNTs) in liquid crystals (LCs) and electro-physical characteristics of LC + CNT suspensions were studied in a very broad range of CNT concentrations, *C*, from 10^{-5} wt% (highly diluted suspensions) to 2.5 wt% (highly viscous suspensions). Along with the conventional sandwich cells with the transparent electrodes on the substrates, we used the cells with the in-plane applied electrical field in order to monitor changes of electrical parameters in the same direction as the structural changes observed under an optical microscope. The data revealed four stages of structural evolution with the increase of *C*: (1) dispersion of individual CNTs and their very small aggregates ($C < 3 \times 10^{-4}$ wt%), (2) presence of branched aggregates with a non-compact structure ($C = 3 \times 10^{-4} - 5 \times 10^{-3}$ wt%), (3) percolation of non-compact aggregates ($C = 5 \times 10^{-3} - 10^{-1}$ wt%) and (4) compaction of aggregates and formation of a dense network ($C = 10^{-1} - 1$ wt%). In the studied concentration range, the conductivity displayed two percolation thresholds at $C_{\rm p}^1 \approx 0.004$ wt% and $C_{\rm p}^2 \approx 0.5$ wt%, which are associated with the formation of a non-compact and dense CNT network. By contrast, the permittivity ε' revealed only one percolation threshold at $C_{\rm p}^2 \approx 0.5$ wt%, when the distance between the adjacent CNTs becomes incredibly small.

These and other effects crucially depend on the structural organization of the nanotubes, which goes through some stages with the increase of CNT concentration and culminates in the formation of a percolation network. In contrast to polymers,¹⁵ percolation phenomena in LC suspensions of CNTs are studied fairly sparingly.^{1,3,16–19} In these studies, attention was mainly focused on the percolation behaviour of electrical conductivity of the LC + CNT suspensions based on various nematic LCs in different alignment configurations. The main results of previous studies are as follows. First of all, the changes in the conductivity of LC-CNT suspensions in the percolation point are not very large: while in the polymer dispersions the conductivity increases on 6-12 orders, in LC dispersions it changes only on 2-3 orders. This is due to noticeable conductivity of LCs because of which they can be considered as weak electrolytes rather than typical dielectrics.

Recently, a two-step percolation transition has been detected by extending the upper limit of CNT concentration and using the appropriate sample preparation with high loading of CNTs.²⁰ The critical concentration of the first stage in the percolation transition, conditionally called dynamic,^{21,22} was very small $(10^{-4}-10^{-3} \text{ wt\%})$, which was explained by the ability of the nanoparticles to move and agglomerate in a low viscous LC medium.²⁰ In the dynamic percolation the transition from the insulating to conductive state is explained by the dynamic

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formation of a conductive network of interconnected CNT agglomerates. The second percolation concentration was of the order of 0.5 wt%.²⁰ As well as in the polymer suspensions²³ it was assigned to the static percolation stage, *i.e.*, to the network formation under the conditions of restricted motions. The observed behavior was explained on the basis of mean-field theory assuming the core–shell structure of CNTs.²⁰ Even in the second stage of percolation the conductivity showed some weak dependence on the temperature and phase state of LC. Therefore, the possibility of further stages of percolation with a further increase of CNT concentration due to strengthening of the contacts between the CNTs has been suggested.

Note that the complex two-step (double), several step (multiple) and even fuzzy (smeared) percolation transitions are rather typical and have been frequently observed in different hosts doped by conducting nanoparticles. The complex mechanisms of percolation were attributed to the local variations in filler particle concentration and/or irregularities in shape and orientation of particles,^{24,25} the presence of different types of particles inside a composite,^{26,27} the existence of different types of electrical contacts,²⁸ selective distribution of conducting particles in the multi-component media,^{29–31} and the existence of static and kinetic network formation processes.³²

While in the previous studies we looked at a range of large CNT concentrations $(10^{-3}-3\%)$ that allowed us to discover the multi-stage character of conductivity percolation,^{1,20} in this paper we consider a wider range of concentrations, including a very low concentration (5 \times 10⁻⁵–2.5 wt%). Our purpose is to investigate the stages of evolution of dielectric characteristics preceding the percolation process. It is in fact the range of concentrations most frequently used in academic research of LC + CNT composites to minimize the distortion of the LC director by aggregated nanotubes.^{5,6} Along with traditional sandwich cells, we involve the cells with in-plane application of the electric field. This cell geometry allowed us to monitor changes in the dielectric characteristics in the same spatial direction as the changes in the micro-structure observed under an optical microscope. Finally, in addition to electric conductivity we analyse percolation features of the dielectric constant. It is demonstrated that the evolution of the dielectric characteristics of LC + CNT suspensions with increasing CNT concentration is closely related to the structural evolution in the system.

2 Experimental

2.1 Materials

The commonly known nematic LC 5CB (Merck) with the crystal-tonematic transition at T = 22.5 °C and the nematic-to-isotropic transition at T = 35.5 °C was used in this study. As CNTs we used short multi-walled carbon nanotubes from Cheap Tubes Inc (Cambridgeport, VT, USA) prepared by chemical vapour deposition and purified using concentrated acid. The CNTs have the length of 0.5–2.0 µm, the outer diameter of 10–20 nm, the inner diameter of 3–5 nm, the specific surface area of ≈ 233 m² g⁻¹, the electrical conductivity > 100 S cm⁻¹, and true density $\rho = 2.1$ g cm⁻³.

2.2 Preparation of the samples

The 5CB + CNT suspensions were obtained by mixing appropriate weights of CNTs with 5CB at T = 60 °C (isotropic phase) and subsequent 10 min sonication using an ultrasonic disperser at 22 kHz and 250 W. The volume fraction of CNTs in the composites φ was evaluated as

$$\varphi = (1 + (1/C - 1)\rho/\rho_{\rm o})^{-1} \approx C\rho_{\rm o}/\rho \approx 0.5C$$
 (1)

where $\rho_0 = 1.02 \text{ g cm}^{-3}$ is the density of 5CB.³³

An investigated range of weight concentrations $C = 5 \times 10^{-5}$ -3.0 wt% corresponds to the range of volume concentrations $\varphi = 2.5 \times 10^{-5}$ -1.5 vol%.

2.3 Methods

Two types of cell geometries were used. Along with conventional sandwich-type cells with the electric field applied out of plane, *i.e.*, perpendicularly to the suspension layer (OP cells), the cells with the in-plane field application (IP cells) were fabricated. The advantage of the second type of cell (IP cells) is that the electrical parameters are measured in the same direction as the structural changes observed under an optical microscope.

The sample preparation procedure is as follows. Two glass substrates (IP cells) or glass substrates with transparent ITO electrodes (OP cells) were covered with the layers of polyimide AL3046 (JSR, Japan) designed for planar alignment. The spin coated polyimide films were properly backed and rubbed by a fleecy cloth in order to provide a uniform planar alignment of LC in the field-off state. The cells were assembled in the antiparallel rubbing directions of the opposite aligning layers. In the case of OP cells the cell gap d was maintained by 50 or 250 μ m glass bead spacers, while in IP cells it was determined by 50 µm thick copper foil stripes used as electrodes. In the latter case (IP cells), the inter-electrode distance h was adjusted to 200 µm. All cells were filled by placing a drop of suspension on one substrate and covering it by another substrate, pressing the substrates together by clamp and gluing by an epoxy. The sketches of IP and OP cells are presented in Fig. 1a and b, respectively.

The macroscopic alignment of the LC fraction of the suspension layer was tested using a light box and two sheet polarizers, while the alignment on the microscopic scale was studied using an optical polarization microscope Polam L-213M. The same device was used to observe a micro-structure of CNTs in LC. This microscope was conjugated with a digital camera for taking static and dynamic images and displaying them on the monitor of a computer.

The dielectric measurements were performed using an oscilloscopic method³⁴ using the parallel connected R - C circuit as an equivalent scheme of the cell. The sine-like voltage with an amplitude of 1 V and a frequency change in the range of $f = 10-10^5$ Hz was applied to the cell. The dynamic volt–ampere characteristics were acquired using an oscilloscope for each frequency, and based on them the cell capacity *C* and resistance *R* were estimated. In turn, these data were used for the calculation of real ε' and imaginary ε'' parts of complex



Fig. 1 Construction of IP (a) and OP (b) cells for microscopic observation and dielectric measurements.

dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$. The exemplary dielectric spectra $\varepsilon'(f)$ and $\varepsilon''(f)$ are presented in Fig. 2.

Based on ε'' data, the sample conductivity σ was determined using the formula $\sigma = 2\pi\varepsilon_0\varepsilon''f$, in which ε_0 is a dielectric constant of free space. This estimation was made at frequency f = 1 kHz, which corresponds to a linear part of the double logarithmic plot of $\varepsilon''(f)$ curves with a slope of -1 (Fig. 2b). This means that electrical conductivity σ in this range, same as dielectric constant ε' (Fig. 2a), are frequency independent. The all measurements were done in the nematic phase at the temperature of 24 °C.

2.4 Statistical analysis

Each measurement was repeated at least three times for the calculation of the mean values and root-mean-square errors. The error bars in all figures correspond to the confidence level of 95%.

3 Results and discussion

First of all, note that the results obtained for IP and OP cell geometries were quite similar. So in the following we mainly focus on the results for the IP series, whereas the part of data for the OP series is given in the ESI.[†]

First, we consider the evolution of structure with an increase in the concentration of nanotubes. Fig. 3 compares microphotographs of 5CB + CNT suspensions in IP cells at different concentrations of CNTs. The small aggregates of the nanotubes with a size of 0.5–2 μ m became visible at the concentration



Fig. 2 Frequency dependences of the real ε' (a) and imaginary ε'' (b) parts of the complex dielectric constant of 5CB + CNT suspensions at three different concentrations of CNTs. Filled squares and unfilled rectangles correspond to the IP and OP series of the samples, respectively.



Fig. 3 Microscopic images of the layers of 5CB + CNT suspensions with different concentrations of CNTs observed under the polarizing microscope at the parallel polarizer and the analyzer. IP series of samples.

 $C \approx 1 \times 10^{-3}$ wt%. The subsequent increase in concentration led to branching of the aggregates, their overlapping and the formation of a continuous network at $C \approx 5 \times 10^{-3}$ wt%. Owing to the spatial confinement inside the cell, a further increase of *C* within the range $5 \times 10^{-2} - 5 \times 10^{-1}$ wt% resulted in compaction of the percolating structure of CNTs. At concentrations above 0.5 wt% the densely packed CNTs fill the entire field of view observed under an optical microscope. The same stages of structural changes were observed for the OP series of samples (see ESI,† Fig. S1).

Fig. 4 shows the concentration dependencies of the electrical conductivity σ (a) and permittivity ε' (b) of the 5CB + CNT suspensions. The first thing to note is that the corresponding dependencies for IP and OP series were practically the same (within an experimental error). Four different types of behaviours of $\sigma(C)$ and $\varepsilon'(C)$ curves can be distinguished. At very low concentrations ($C < 3 \times 10^{-4}$ wt%, range I) the initial jumps



in σ and ε' values were observed (see, insets). These jumps can be related to the domination of individual (non-aggregated) CNTs in the suspensions.

An extended Maxwell approximation predicts a linear concentration growth of electrical conductivity of the composite medium filled by randomly oriented and arbitrarily shaped conductive particles in the limit of a very low volume fraction:³⁵

$$\sigma = \sigma_{\rm o} (1 + [\sigma] \varphi) \tag{2}$$

where σ_0 is the electrical conductivity of the host medium (LC medium in our case) and $[\sigma]$ is the coefficient known as the intrinsic conductivity that can be rather high for a filler with an anisometric shape.

Fitting of our experimental data at low concentrations $(C < 3 \times 10^{-4} \text{ wt\%})$ using eqn (2) gives $[\sigma] = 4900 \pm 1500$. The theory predicts strong dependence of the $[\sigma]$ value on the particle aspect ratio r (*i.e.*, the ratio of particle length to its diameter). Using the tabulated values of $[\sigma]$ for prolate ellipsoids (Table 1 in ref. 36) one can plot the curve $[\sigma](r)$ (see ESI,† Fig. S2) and then by fitting can find the following analytical expression:

$$r \approx 2.75 [\sigma]^{0.543}$$
. (3)

By setting $[\sigma] = 4900 \pm 1500$ in eqn (3) one can get $r = 280 \pm 50$. This value is close to the value r = 50-200 which can be directly derived by taking values 500–2000 nm and 10–20 nm for the length and diameter of the studied CNTs, respectively. It should be noted that for conducting spherical inclusions Maxwell theory predicts a rather small value of $[\sigma] \approx 2.5$.

In the concentration range II ($C = 3 \times 10^{-4} - 5 \times 10^{-3}$ wt%) the electrical conductivity only slightly increased with *C* (Fig. 4a). This may reflect the stage of strong aggregation, further branching and shape isotropization of the aggregates.

The further increase of concentration within the concentration range III ($C = 5 \times 10^{-3} - 1 \times 10^{-1}$ wt%) resulted in a steep increase of the electrical conductivity typical of percolation processes. This increase evidently reflects the formation of a branched inter-penetrating network of non-compact aggregates. With the further increase of the concentration within the range IV (C = 0.1-1 wt%) the second steep increase of the $\sigma(C)$ curve was observed that reflected the additional stage of conductivity percolation (Fig. 4a). According to Fig. 3, it can be associated with the compaction and restructuring of CNT clusters forming the percolation structure owing to the spatial confinement inside the cell. This compaction resulted in the improvement of the electrical contacts between individual CNTs that affected the conductivity percolation.

The $\sigma(C)$ curve in the concentration range of each percolation step was well fitted to the percolation scaling law³⁷

$$\sigma \propto (C - C_{\rm p})^t \tag{4}$$

Fig. 4 Electrical conductivity σ (a) and permittivity ε' (b) versus concentration of CNTs *C* in 5CB + CNT composites. The concentration ranges I, II, III and IV correspond to different behaviours of $\sigma(C)$ and $\varepsilon'(C)$ curves. Filled squares and unfilled rectangles correspond to the IP and OP series of the samples, respectively. The insets show the concentration behaviour of the corresponding parameters at C < 0.005 wt% for the IP series of samples.

where $C_{\rm p}$ and t are the percolation concentration and the electrical conductivity transport exponent, respectively. The fitting parameters are $C_{\rm p}^1 \approx 0.004$ wt% and $t_1 \approx 0.33$, and $C_{\rm p}^2 \approx 0.5$ wt% and $t_2 \approx 0.07$ for the first and second percolation steps, respectively.

The first percolation threshold C_p^1 is very low, which is quite common for highly anisometric nanoparticles in dispersing media with low viscosity.¹⁵ In this case, nanoparticles have sufficient kinetic energy to surmount the potential barrier between them and agglomerate in a process of diffusion and thermal jostling. Since LCs possess sufficient amounts of ions, this barrier can be reduced due to partial compensation of nanoparticle charges and thus weakening of the electrostatic repulsion between them. This further facilitates agglomeration and lowers the value of C_p^1 .

The second percolation stage is characterized by the threshold at C_p^2 , which is three orders of magnitude higher than C_p^1 . At concentrations in the vicinity of C_p^2 the suspension becomes very viscous so that it can be loaded in the cells only by using a drop pressing method. We believe that the applied pressure improves the electrical contacts between the CNTs that eventually leads to the second percolation stage.

The estimated transport exponents t_1 and t_2 are fairly small compared with those theoretically predicted in statistical theory for the three-dimensional ($t \approx 2$) and two-dimensional (t = 4/3) percolation problem.³⁷ These small values may be associated with the essential electrical conductivity of LCs that makes theoretical results obtained for the combination of the conducting filler and the dielectric matrix not quite applicable for the LC dispersions. According to ref. 38, decreasing the jump of electrical conductivity in the percolation point affects the slope of the $\sigma(C)$ curve in the vicinity of this point (see the ESI,† Section S3).

As can be seen in Fig. 4, this is exactly the case of our samples in which the conductivity jumps only two orders of magnitude with a gradual growth in a rather wide range of C. In other words, the percolation transition in this case can be attributed to the category of smeared transitions with the discernible two-stage structure. This may cause an essential deviation of the experimental value of t from the one predicted theoretically.

Thus, the complex change of the course of the $\sigma(C)$ curve in the percolation area is determined by the efficiency of electrical contacts of the adjacent nanotubes, which increases with *C*. Based on this the so-called core–shell model³⁹ was proposed which assumes that the CNTs consist of a highly conductive core and a less conductive shell and considers transition from weaker (shell–shell) to stronger (core–core) electrical contacts between the nanotubes with increasing CNT concentration. In the frame of this model the two-step character of the $\sigma(C)$ curve of the LC–CNT system was recently interpreted in ref. 20.

The concentration dependence of the effective permittivity ε' is shown in Fig. 4b. The following features can be noted:

(1) A giant increase of the permittivity; the value of ε' grows by two orders of magnitude when *C* changes from 0 to 1 wt%. Such a giant dielectric response is fairly common for the dispersions of conducting particles in insulating matrices⁴⁰ including dispersions of CNTs.^{41,42} In all these systems divergence of the curve $\varepsilon'(C)$ below the percolation threshold at $C \leq C_p$ was successfully fitted to the following power law:

$$\varepsilon' \propto (C_{\rm p} - C)^{-s}$$
 (5)

where $C_{\rm p}$ and *s* are the percolation threshold and the electrical permittivity transport exponent, respectively.

A rapid increase of ε' when *C* approaches a percolation point can be explained by the formation of a network of microcapacitors formed by the neighbouring particles and a thin dielectric layer in between.⁴³ The system of these elementary capacitors forms an abnormally large capacitance of the composite layer, hence the high ε' is expected. Different resistorcapacitor network models have been developed for studying this effect.^{44–47}

(2) For our system the divergence of effective permittivity ε' was only observed in the vicinity of the second percolation transition, *i.e.*, at concentrations below C_p^2 . The fitting of the experimental curve $\varepsilon'(C)$ in this concentration range to eqn (4) gives $C_p^2 \approx 0.5$ wt% and $s \approx 1.6$. The obtained value of parameter s is greater than the values predicted by theory $(s = 0.8-1.3^{40,48})$ the same as the experimental values for the polymer dispersions of CNTs ($s = 1.05 - 1.23^{49}$). This may be partially caused by the specific nature of LC dispersing media discussed above. The insensitivity of ε' to the first percolation step of σ (Fig. 4) may be explained by the fact that the interparticle distance in the case of a branched network in the vicinity of C_p^1 is large so that capacitances of the elementary capacitors are too low. The situation changes by approaching the region of dense network, *i.e.* at $C \rightarrow C_p^2$. Here, the gaps between the particles become small while their capacitance becomes sufficiently high. These elementary capacitors accumulate significant charges that greatly enhance the local electrical fields. When the adjacent particles further approach each other, these charges relax; first by tunnelling (when the tunnelling distance is achieved) and then by the ohmic mechanism (when the particles touch each other directly).

To shed light on the real physical mechanisms of charge transfer, which are behind the "shell–shell" and "core–core" states of inter-particle contacts, the frequency dependencies of electrical conductivity derived from dielectric spectra were analysed. The family of the $\sigma(f)$ curves corresponding to different CNT concentrations is shown in Fig. 5a. It is evident that the course of the $\sigma(f)$ curve strongly depends on CNT concentration. For pure LC and the composites with low loading of CNTs (C < 0.005 wt%) the value σ was practically independent of f in the selected frequency range $10-10^4$ Hz. With a further increase of C from 0.005 wt% to 1 wt% the $\sigma(f)$ curves demonstrate a pronounced growth. Finally, at C > 1 wt% these curves become frequency independent again in the mentioned frequency range.

As in the case of polymer composites of CNTs,⁵⁰ the $\sigma(f)$ curves were fitted to the universal dynamic response law

$$\sigma = \sigma_{\rm DC} + A f^m, \tag{6}$$

where the first term σ_{DC} corresponds to the low frequency limit of electrical conductivity and the second term in the form of power function describes a frequency dependant part, where the exponent *m* is in the range of 0–1.

The *m* versus f plot is presented in Fig. 5b. It can be seen that the m(f) curve demonstrates a two-stage growth and a



Fig. 5 (a) Electrical conductivity σ versus frequency f curves for the 5CB + CNT composites with various concentrations of CNTs C. (b) Frequency exponent *m* versus concentration of CNTs C. OP series of samples.

subsequent abrupt decrease at $C \ge 1.5$ wt%. It is noteworthy that the first and the second increase start roughly at percolation concentrations C_p^1 and C_p^2 meaning that the exponent *m* is sensitive to both steps of percolation transition.

Note that the power-law dependence $\sigma(f)$ (eqn (6)) can reflect hopping and/or tunnelling mechanisms of the charge transfer between the neighboring nanotubes.¹⁷ The transition from the first to the second growing stage of the m(f) curve at $C \approx C_p^2$ reflects the transition from the branched (range III) to dense (range IV) CNT networks and may be accompanied by the transition from the dominating hopping to the dominating tunnelling mechanism of conductivity. The decrease of m to 0 at $C \ge 1.5$ wt% may be caused by the further strengthening of inter-particle contacts and the transition to the domination of the ohmic conductivity mechanism similar to the pressed nanotubes with a very weak frequency dependence. The frequency independent term σ_{DC} at low concentrations of CNTs (C < 0.005 wt%) can be mainly attributed to the ionic conductivity of the LC matrix. The further increase of this term with C may be caused by additional ions released from the surface of CNTs and the conductivity of channels created by the strongly contacted nanotubes (contribution of the mechanism, which dominates at $C \ge 1.5$ wt%).

Finally, we discuss the possibility of the alignment of CNTs in LC matrices. The alignment of these particles and their small aggregates imposed by the orientational order of LC was previously reported.^{51,52} In the vast majority of publications the concentration of CNTs fell into the range I ($C < 3 \times 10^{-4}$ wt%). According to Fig. 2, when *C* approaches the first percolation point at C_p^1 , the aggregates of CNTs grow and branch becoming more isotropic. The randomization of CNTs is even more enhanced after the first stage of percolation.

On alignment of CNTs in LCs are pinned the hopes of experimental verification of theoretical predictions about the dependence of percolation concentration on the degree of ordering of CNTs. Intuitively, high ordering of CNTs destroys the percolation pathways created by intersected nanotubes and thus decreases electrical conductivity. However, Monte Carlo simulations indicated that maximal conductivity can be achieved for slightly aligned rather than for randomly distributed CNTs.⁵³ Our results demonstrate that it is difficult to check this rule using conventional nematic LCs, because randomization of CNTs occurs earlier than the percolation structure is formed. However, the conditions can be better when using other LC



Fig. 6 Illustration of changes in the structure of 5CB + CNT suspensions with concentration of CNTs C revealed from microscopic and dielectric studies.

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phases with more favourable visco-elastic characteristics. The improvement of CNT alignment may also be achieved by means of external action on the composite layers, such as shear, electric or magnetic fields, $etc.^{54-56}$ The influence of these factors on the degree of orientational ordering of CNTs and the parameters of their percolation is an interesting problem for future research.

4 Conclusions

In conclusion, the structural and dielectric properties of the suspensions of CNTs in nematic LC 5CB with the CNT concentration varied in a very wide range 10^{-5} –2.5 wt% have been investigated. The suspensions were filled in flat capillary cells with the application of electric voltage in-plane or perpendicularly to the cell plane.

The data revealed four different concentration ranges for 5CB + CNT suspensions that correspond to different types of structural organizations schematically presented in Fig. 6:

Range I. At $C < 3 \times 10^{-4}$ wt% the samples contain individual CNTs and their very small aggregates.

Range II. In the range $C = 3 \times 10^{-4} - 5 \times 10^{-3}$ wt% one can see the formation and growth of separated aggregates with a branched (non-compact) structure.

Range III. In the range $C = 5 \times 10^{-3} - 10^{-1}$ wt%) one can see the overlapping of branched CNT aggregates and the formation of percolation clusters.

Range IV. Finally, at $C = 10^{-1}$ -1 wt% compaction of aggregates and formation of a dense CNT network are observed.

The dielectric parameters perfectly correlate with the described structural changes and demonstrate the same stages. The rapid increase of conductivity within the first concentration range can be explained using the Maxwell theory for anisometric particles with the aspect ratio $r = 280 \pm 50$. Deviation from this behaviour in range II is explained by intensive aggregation of CNTs. The following two ranges III and IV correspond to two stages of conductivity percolation with critical concentrations $C_{\rm p}^1 \approx 0.004$ wt% and $C_{\rm p}^2 \approx 0.5$ wt%. Transition from the first to the second step of percolation reflects transition from the non-compact to compact arrangement of CNTs within the percolation cluster and, presumably, the change of the dominating mechanism of charge transfer through the CNT structure. In contrast to the electrical conductivity σ , effective permittivity ε' revealed the single-stage percolation behaviour with a threshold at $C_p^2 \approx 0.5$ wt%, *i.e.*, in the range IV within which the distance between adjacent CNTs significantly decreases.

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