

# Nano-carbon in a hydrogel matrix for nonlinear optical applications



Alexandra L. Nikolaeva<sup>a</sup>, Andrey Yu Vlasov<sup>a,\*</sup>, Ivan M. Kislyakov<sup>b</sup>,  
Vladimir Yu Elokhovskiy<sup>c</sup>, Ivan M. Zorin<sup>a</sup>, Svyatoslav A. Povarov<sup>b</sup>

<sup>a</sup> Institute of Chemistry, St.Petersburg State University, 198504, St.Petersburg, Russia

<sup>b</sup> International Laboratory of Nonlinear Optical Informatics, ITMO University, 197101, St.Petersburg, Russia

<sup>c</sup> Institute of Macromolecular Compounds, Russian Academy of Sciences, 199004, St.Petersburg, Russia

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## ABSTRACT

We report on the optical power limiting properties of nano-sized carbon (single walled carbon nanotubes and carbon black) embedded in an aqueous-polymer matrix in the phase state of a hydro-gel. A polymer employed is Pluronic F-127, who simultaneously features as a stabilizer of the nano-carbon in a fluid water-polymer medium. Limiting thresholds of the composites are given in a bijection with a phase diagram (determined by DSC, rheometry and vibrational viscometry) of a matrix alongside its viscous characteristics and caloric properties of phase transitions involving the gel and micellar solution. Reversible gel-to-isotropic fluid transition of the matrix renders optical material thermo-healing with regard to optical breakdowns inflicted by high-intensity laser irradiation in the solid-like gel state.

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## 1. Introduction

During recent years perspective applications for optically transparent condensed systems containing various nano-particles (nano-carbon, nano-metals, quantum dots, etc.) have been developed, *i.e.* non-linear optical power limiting (OPL) [1]. OPL consists in a drastic attenuation of light upon propagation through a material provided an incident light intensity surpasses a critical value termed a limiting threshold. This phenomenon is anticipated to be used for protection of sensors and the human eye against high intensity laser irradiation. The protecting OPL devices should comply with a number of requirements, *viz.*: optical transparency to low intensity light; sensitivity and fast non-linear response to an intense light irradiation; sufficient phase stability in the working environment and resistivity regarding disruption by high intensity irradiation.

Investigation of the nano-carbon OPL properties is closely related to a search for a dispersing medium appropriate for the specific use. Recently, fluid aqueous suspensions of nano-carbon have been extensively studied and applied [2,3]. Different kinds of films [4], crystalline colloidal arrays [5] and glasses [6,7] have also been reported to be germane matrices for photo-active

particles. However, there are some issues with a design of practical optical materials operating with high-intensity radiation: *viz.*, fluid-state ones are not universally relevant for practical use, whilst, on the other hand, in the solid-state material there evolve incurable disruptions in the vicinity of a focal volume of high-intensity laser beam, thereby protective properties of the system are handicapped therein.

In the present investigation we gave a go to sort out drawbacks of the said phase states of the matrix, employing aqueous suspensions of either single-walled carbon nano-tubes (SWCNT) or carbon black (CB) suspensions, dispersing media being made rigid by Pluronic F-127 so as to provide the hydro-gel. This amphiphilic polymer also featured as a stabilizing micro-environment for nano-carbon in water [8–10]. It is also worth mentioning that gel materials based on Pluronic F-127 are so viscous and stiff that even heavy particles can be suspended without subsidence on a long time-scale [11–13].

Pluronics are nonionic tri-block copolymers poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) [(EO)<sub>m</sub>(PO)<sub>n</sub>(EO)<sub>m</sub>] with surfactant functionality [13–16]. Aqueous solutions of Pluronic F-127 have the simplest phase behavior and have been investigated by a number of techniques, including rheometry [11–13], small-angle neutron scattering (SANS) [12,13], differential scanning calorimetry (DSC) [13,15,17], light scattering (LS) [17], etc. A phase diagram as it comes from a number of sources is given in Fig. 1. It is

\* Corresponding author.

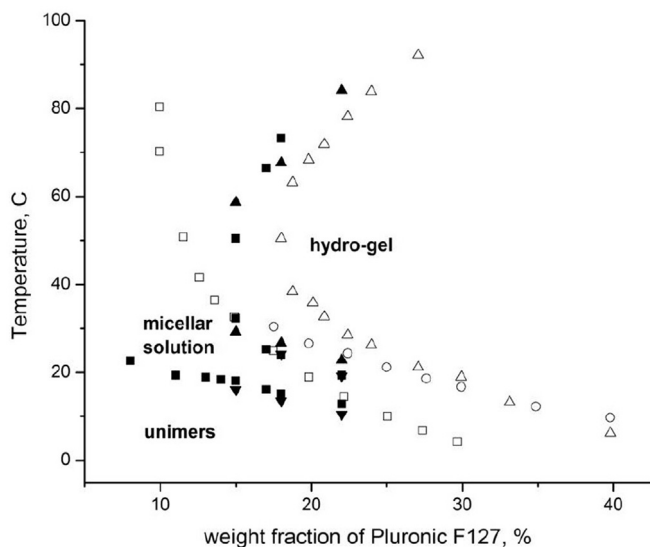
E-mail address: [drew-v@yandex.ru](mailto:drew-v@yandex.ru) (A.Y. Vlasov).

ascertained that in dilute solutions and at low temperatures Pluronic F-127 exists in the form of free unimers. Above a certain temperature it aggregates into micelles owing to changing  $(PO)_n$ -part conformation which causes an increase of hydrophobicity of the latter [18]. With a further increase of temperature spherical micelles composed of hydrophobic  $(PO)_n$  core and hydrophilic  $(EO)_m$  corona form an optically transparent hydro-gel [11,19,20]. The hydro-gel formed is two-fold thermo-reversible: it undergoes an isotropic solution-to-gel transition on the lower boundary of the gel domain in the phase diagram and a re-entrant transition to a phase state with viscosity lower than in the gel, thereby resembling a liquid-like one at higher temperatures [11,14]. Formerly hydrogels have been employed as matrices for the OPL materials quite seldom. In Ref. [21] chitosan hydrogels are reported to possess self-healing abilities of structural defects caused by laser irradiation. However, this property is inherent to materials with low volume fraction of the polymer (ca. 2%), the system being almost a liquid. This defines low mechanical, thermo-optical and strength characteristics of the material. In the work [22] graphene sheets were embedded in hydro-gel of polyvinyl alcohol, healing of the system after an optical damage was attained by heating it up to the temperature of 60–80°C and conversion into liquid with subsequent reverse transition into the gel.

Following the state-diagram of the water – Pluronic matrix [13,17,19] we processed gel-state suspensions of SWCNTs and CB and studied their OPL characteristics (a limiting threshold, a limiting factor and a break-down intensity) alongside possible rejuvenation of the OPL functionality by temperature-induced phase transitions into isotropic liquid suspensions. The property of hydro-gel thermo-reversibility casts scenarios for processing prototype solid self-healing materials, which can be used in various optical applications. Note in passing, regeneration of purpose functionality of optical materials also stands in the field of optical data storage [23].

## 2. Materials and methods

The tri-block copolymer, Pluronic F-127 ( $M_w = 12.6 \cdot 10^3$ ) was purchased from Sigma Aldrich and used as received. It is stated that,



**Fig. 1.** Phase diagram of Pluronic F-127 in water. Open signs are data from literature [17]: – circles [13], – squares [19], – triangles. Filled signs designate the data of the present study: DSC – triangles (vertices down), viscosimetry – squares, rheometry – triangles (vertices up).

take away some properties (e.g., surface tension), the fractionalized and the un-fractionalized samples of this polymer have virtually the same phase behavior [24]. We used distilled water for processing aqueous polymer mixtures, because it has been shown [18], that whether it is  $D_2O$  or a distilled  $H_2O$ , neither gelation nor micelization lines in the state space of a binary system are affected.

We used CB (Carbon nano-powder from Sigma Aldrich, purity claimed by a Producer > 99%), whose crystallites had linear dimensions not surpassing 50 nm. HiPCO SWCNTs were purchased from Carbon Nanotechnologies Inc., Houston, TX, with purity 85%. To process suspensions, a weight dose of Pluronic F-127 (5 wt%) for stabilizing nano-carbon was placed in water, wherein certain amounts of nano-particles (SWCNTs or CB) were added: SWCNTs – 0.03 wt%, CB – 0.3 wt%. Blends gotten underwent ultra-sonic processing: the power of a tip employed was ca. 1 kW, a regime of processing included two periods of 15-min duration with 15-min break between them. Ultra-centrifugation was performed differently for suspensions with different nano-particles: SWCNT suspensions were processed with Sorvall WX Ultra Series (Thermo Scientific; rotor T 890, 50000 rpm, 1 h duration), CB dispersions with LMC-4200R (Biosan, Latvia; 4000 rpm, 20 min duration). Supernatants for preparing samples were taken in both cases as 2/3 of the total vial volume (4 ml). This sort of mechanical processing ensured removal of catalysts remnants and admixtures of alternative allotropic carbon modifications from the samples, also providing higher fractions of isolated nano-tubes, their smaller fine bundles and smaller particulars of CB. Our previous Cryo-TEM monitoring of the mechanical processing impact on the degree of SWCNT aggregation in the suspensions stabilized by common surfactants [25] indicated that using of the aforementioned ultra-sonication/ultra-centrifugation procedure ensured an average diameter in the SWCNT populace of the feed suspensions equaling to ca. 2 nm and a contour length – ca. 150 nm. As it concerns the size of CB particulates, dynamic LS (Zetasizer Nano ZS, Malvern Instruments) observations showed distribution of nano-carbon particles in the interval 40–50 nm. In the present work we did not set a specific assignment of varying the size of nano-carbon in transparent condensed-state matrices with an aim to get its correlation with OPL parameters, insofar as principal phenomenology of this dependence in SWCNT dispersions was addressed in our previous work [3]. Main trends concerning non-linear optical effects in fluid suspensions containing CB particles with varied sized were also discussed elsewhere [26,27]. Preparation of the gel-forming compositions consisted of mixing weighed amounts of the polymer and water followed by allowing equilibration for about a week depending on the copolymer concentration at temperatures +4 – +6 °C. Then an appropriate dose of carbon nano-material suspension was added to the system obtained. After stirring, the tubes were kept in a refrigerator for a couple of days before measurements.

Characterization of suspensions and hydro-gels containing nano-carbon was performed by absorption spectroscopy (Lambda 950 Perkin Elmer, quartz cuvettes, path length 1 cm, wavelength interval 250–900 nm). Fig. 2 exemplifies the obtained spectral lines of hydro-gels. For the SWCNT system one can easily distinguish peaks corresponding to the band-gap optical transitions, characteristic for the HiPCO nano-tubes [28]. Spectrum of CB gel shows smooth broadband absorption. Maxima ( $\lambda \approx 270$  nm) for gels with both morphologies correspond to  $\pi$ - $\pi^*$  molecular orbital transition, intrinsic to  $sp^2$  hybridized carbon bonds.

As is seen in Fig. 1, there is no complete consistence regarding location of the state domains in the phase diagram “Water + Pluronic F-127” between the sources [13,17,19]. Discrepancies may stem from a number of origins, viz., a batch of the polymer, its molecular mass, peculiarities of methodologies

employed.

In order to establish phase behavior of the Pluronic F-127 aqueous mixtures and to evaluate the effect of the carbon nano-material on the phase transitions of micellization and hydro-gel formation we prepared a number of solutions (8–25 wt% of the polymer). All samples were placed into measuring cells at low temperature (5 °C) and then poly-thermally monitored. We determined phase transitions (micellization, gelation and a reverse transition from the gel to the isotropic fluid) by 3 methods. Rheological measurements were performed by a rheometer Physica MCR 301 (Anton Paar) with a cylinder configuration CC17. Oscillatory measurements were done in a dynamic mode with a deformation of 1% and frequency 10 Hz within 5–105 °C temperature interval (heating rate 2 °C/min). The DSC measurements were implemented with Setaram  $\mu$ DSC III Evo setup. The steel cell was filled with 1 ml of a cold isotropic liquid sample and then hermetically sealed. Heating of a sample spanned 0–80 °C and was performed with 0.5 °C/min rate followed by subsequent gradual cooling. The cycle was re-iterated twice. The 3rd method employed was vibrational viscometry (viscometer A&D SV-10a operating at 30 Hz frequency).

To study the OPL properties of nano-carbon in binary matrices prepared in the fluid and hydro-gel states we used a frequency-doubled Q-switched Nd:YAG laser (532 nm; pulse duration 7 ns; 1 Hz repetition rate, 8 mm beam diameter). The incident energy was controlled by changeable neutral glass filters and was measured by a setup reported earlier [29]. A 1 cm quartz cuvette with a sample was placed in a focal plane of a condensing lens  $f = 40$  mm. The energy of pulses, passed through the sample was registered in a solid angle of 1.6 mrad by silicon detector. Each energy value was an average from a set of 10 pulses.

### 3. Results and discussion

Apart from the literature data Fig. 1 contains the boundaries of the unimer solution, isotropic micellar solution and the gel such as they are determined in our observations. It is well seen that all of the three methods applied procured agreeing data with regard to all of the phase state domains boundaries. The gel domain is confined by both, the lower and the upper transitions into liquid state, the picture agreeing with Refs. [13,17,19]. In all of the 3 methodologies scanning of temperature has been performed in

both directions, showing no tangible displacements of the observed purpose parameters (viscosity or heat flow) which casts in favor of the thermo-reversible character of transitions unimer – micellar solution, micellar liquid – hydro-gel, hydro-gel – fluid.

Worth a note is that rheological data show extremely steep jumps and drops of viscosity on the boundaries of the hydro-gel phase, the absolute value of the jumps monotonically growing with the polymer content in binary systems (Fig. 3(a)). Fig. 3(b) exemplifies a polythermal line of the dynamic loss  $\tan(\delta)$ , also known as the damping factor (solid line), in the just processed solution of Pluronic F-127 with concentration of 22 wt%. In the gel-state domain this quantity demonstrates a plateau, where values of damping factor are below unity, which is appropriate to hydro-gels of Pluronics [30,31], with sharp maxima spikes circumscribing this plateau on the boundaries. Drastic changes in rheological parameters agree with structural transformations observed by SANS in Ref. [12]. In our observations the isotropic state above the upper temperature boundary in many cases showed the damping factor values slightly or palpably below unity, which is indicative of certain elastic properties of this phase. Temperature evolution in the aqueous systems of Pluronics in the proximity of the upper boundary of the gel state is ascribed either to de-hydration of the micellar EO coronas and a consecutive reduction of Pluronic micelles volume [12], or to a polymorphic transition sphere-to-ellipsoid in the micellar shape weakening the inter-micellar interactions [14].

A set of DSC endotherms for aqueous solutions of Pluronic F-127 (15, 18 and 22 wt%) are shown in Fig. 4. Therein it is seen, that an increase of the polymer concentration results in greater heat effects of micellization: a big peak corresponding to this transition is observable in all of the polytherms, tendencies of the peak evolution being in line with data of Refs. [13,15,32]. Micellization heats registered are: 3.37, 4.49 and 5.33 J/g for 15, 18 and 22 wt% solutions correspondingly. A lower peak adjacent to a micellization one is observable only in the solutions with concentrations 18 and 22 wt%. Juxtaposing its onset temperatures with viscosity and rheology polytherms alongside detailed structural analysis of [12], we presume that this peak corresponds to the isotropic micellar solution-to-gel transition. Insofar as it does not show up on the polytherm of 15 wt% solution, we are prone to suppose that its heat is not detectable within the sensitivity of the DSC run.

As it comes to the response of phase boundaries to the addition of nano-carbon in quantities relevant for optical applications (*vide supra*), the regularities are as follows. The line of micellization stays virtually intact for formulations with both SWCNTs and CB. The lower gelation boundary is shifted down within the margin of 2 °C by SWCNTs and is almost unperturbed by CB. The upper boundary of the gel state in the systems with nano-carbon has not been monitored.

The reciprocals of energy, passed through the sample, vs. incident energy of laser irradiation (limiting curves) in the systems of SWCNTs in binary “water + 18% wt. Pluronic” matrices are shown in Fig. 5(a). Arrows in Fig. 5 point at the limiting threshold values. It is seen that the OPL procured by the matrix *per se* is considerably amplified by small amounts of nano-carbon: say, the limiting threshold is reduced by 2 orders of magnitude. In the interpretation of data in Fig. 5 we embarked from the following paradigm. The photon-excited electronic structure of a nano-carbon particle gets relaxed *via* the channel of vibrational degrees of freedom of the carbon atomic carcass in both CB and SWCNTs [33] and also, when it comes to the metallic populace of nano-tubes, *via* certain  $\pi$ -Plasmon oscillations. In case of CB, phonon relaxation is presumably faster due to highly defective character of the carbon carcass, thereby causing fast plasmatation of particles and/or disruption of valent bonds between atoms [26,34]. This process seems to be

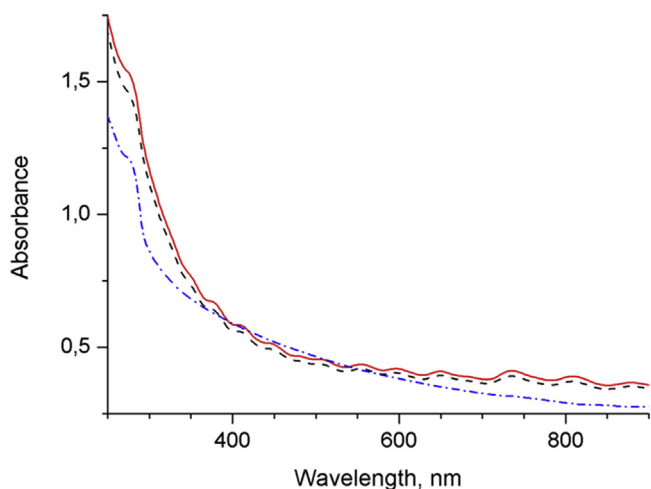
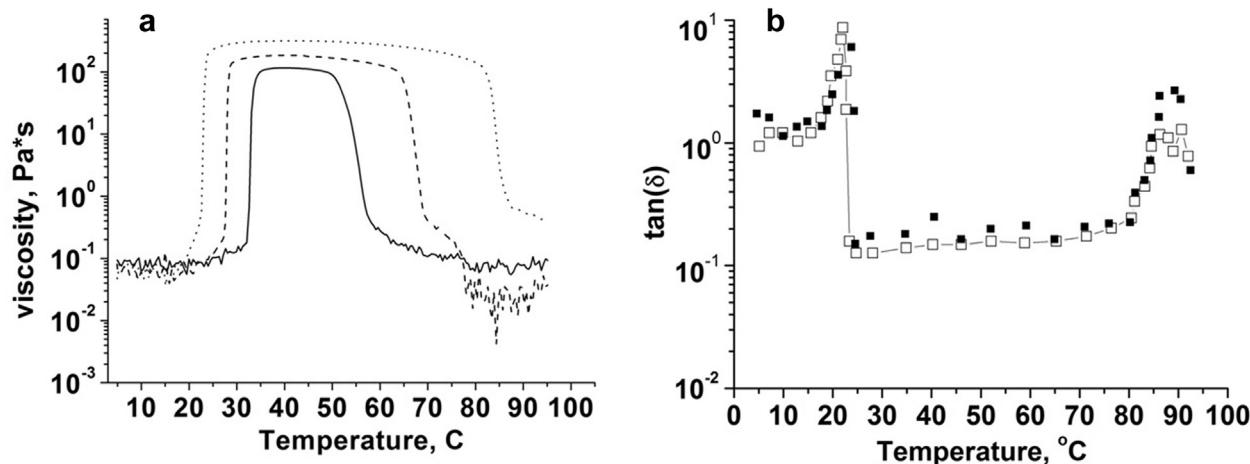
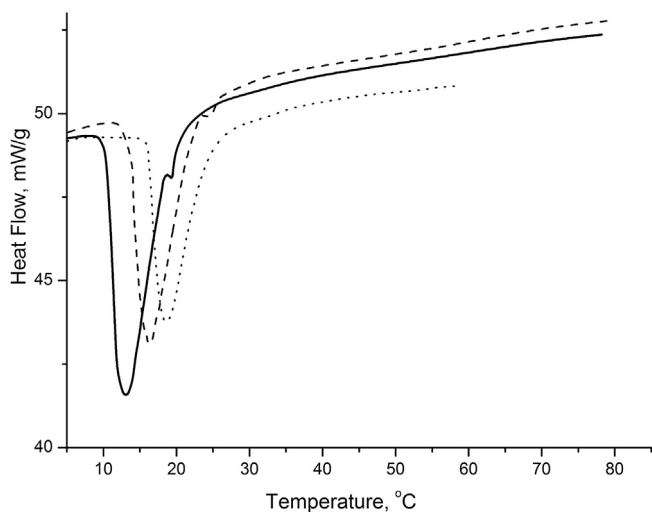


Fig. 2. Absorption spectra of nanocarbon in Pluronic F-127 hydro-gels: SWCNT in the sample just after preparation (solid line), the same sample after 4 months' storage (dashes), CB (dash-dotted line).



**Fig. 3.** (a): Polytherms of viscosity in aqueous mixtures containing 15 wt % (solid line), 18 wt % (dashes) and 22 wt % (dots) of Pluronic F-127. Jumps and drops of the property with an increase of temperature herald phase transitions corresponding: micellar solution-to-gel and re-entrant gel-to-isotropic liquid. (b): Temperature dependency of the damping factor (dynamic loss  $\tan$ ) in an aqueous solution of Pluronic F-127 (22 wt %): empty symbols stand for the sample shortly after processing, filled squares – for the same sample after 4 months of storage at ambient temperature..



**Fig. 4.** DSC endotherms for aqueous mixtures of Pluronic F-127: 15 wt % (dots); 18 wt % (dashes); 22 wt % (solid line).

followed by heat transfer to the medium of micro-environment and the matrix, which is widely supposed to be the leading mechanism of generating inhomogenities (in extreme case bubbles of micro-environment and a solvent). The OPL is performed on the latter by scattering of subsequently incoming photons. In SWCNTs, attenuation of phonons is presumably slower and in a certain interval of incident energy values is implemented in the form of heat transfer to the solvent. Systems with both types of nano-carbon particles demonstrate local boiling of the solvent. This process, we presume, is prevailed by phase transition gel-to-liquid, which complements limiting by scattering on liquid micro-lenses in the gel medium. The upper temperature boundary of the gel domain in the phase diagram makes appearance as an image of an almost athermal phase transition. Unlike rheological polytherms (say, for the damping factor (Fig. 4(b)), where sharp spikes witness the structural transformation), the DSC curves (Fig. 3) for aqueous Pluronic solutions do not show peaks detectable within precision bars of the experiment. Evidently even if this transition (possibly intermingled with ongoing with an increase of temperature

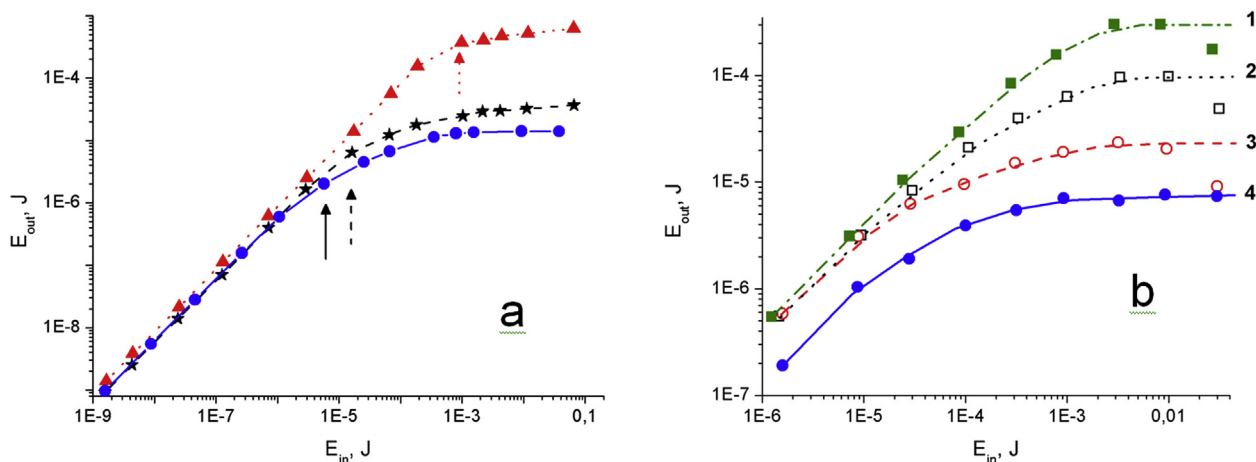
enthalpic de-hydration of the EO corona of Pluronic micelles) has some enthalpic feature, the latter is a small one. Therefore, local sharp transients of temperature on the nano-carbon surface may easily include gel-to-liquid local transition into a succession of emerging inhomogenities, who make an additional increment to non-linear optical scattering. Obviously, upon formation of liquid-state micro-environment, generation of bubbles is the simpler the smaller are the values of surface tension, viscosity and evaporation enthalpy [35]. Fig. 5(a) shows that OPL characteristics of SWCNTs in hydro-gel are pretty commensurable with those of its aqueous suspension stabilized by sodium dodecylbenzene sulfonate (SDBS) despite the fact that hydro-gel viscosity for this polymer concentration (ca.  $2.5 \cdot 10^5$  mPa s) is 5 orders of magnitude bigger than in the liquid water. It implies extremely fast response of the hydro-gel matrix upon local heat influx from nano-carbon resulting in a phase transition into the liquid with successive vaporization.

Measured OPL effects in nano-carbon-containing hydro-gels with different concentrations of Pluronic are shown in Fig. 5(b). The curves indicate averaged dependences; points at highest energies for systems (1–3) decline downwards the curves due to occurrence of optical breakdown. For the dependence 4 no disruptions were observed in the applied energy range most probably because its optical density was too high, and the light was mostly scattered prior to the optical waist. Dependences in Fig. 5(b) give limiting threshold values: 110 mkJ (curve 1), 40 mkJ (curve 2), 18 mkJ (curve 3), and 16 mkJ (curve 4).

Setting aside curve 4 as the one for a system with remarkably higher concentration of nano-carbon, we can note: 1) limiting threshold values are notably higher for SWCNT than for CB; 2) in hydro-gel with SWCNT, the bigger is Pluronic concentration, the lower are threshold values.

The first observation concerns different rate of optical energy conversion into heat in these carbon modifications. A decrement of carbon carcass vibrations in nano-particles is greater given higher concentration of defects. Obviously, CB procures more defects in comparison with almost ideal SWCNTs cylinders. Consequently, the vibrational relaxation and, thereby, heating of both, the nano-particles (with formation of submicro- and micro-plasma) and the proximate solvent, takes place more readily in the system with CB rather than with SWCNTs.

As it comes to the second observation, it can presumably be explained by that, given all the other conditions similar, micro-



**Fig. 5.** (a). OPL in hydrogel matrix with no nano-carbon (triangles, dotted line), in hydrogel with SWCNTs (asterisks, dashed line) and in aqueous dispersion of SWCNTs stabilized by SDBS (circles, solid line). (b) OPL in hydrogels with SWCNT (squares) and CB (circles), concentration of Pluronic: 18 wt % (filled symbols) and 22 wt % (hollow symbols).

bubbles of the solvent are formed the simpler, the smaller is the surface tension of the liquid phase generated by preliminary heat-induced transition gel-liquid, *i.e.* in the system with bigger content of an amphiphile polymer. Yet another aspect of the behavior may be density and viscosity discontinuities between the gel and a local liquid domain around the heated particle: they differ more radically in case of higher concentration of the polymer.

Getting back to curve 4, one notes comparing it with curve 3 that an increase of CB content in the composite does not virtually affect the limiting threshold. This observation is quite consistent with Ref. [36].

Propagation of high-intensity laser irradiation across the hydrogel causes its disruption (break-down) in the focal volume, however, only a small fraction of nano-particles turn out to be burned. A solid-like material disrupted in the said way may be regenerated by its transfer into isotropic liquid (by either heating or cooling in accord with the phase diagram). In the liquid state diffusion of burned particles into the matrix bulk and influx of unperturbed

ones into the former domain of the optical waist rejuvenate the homogeneity of the material (Fig. 6) as well as its OPL abilities. Limiting curves of a pristine material and a material regenerated by phase transition into liquid and reversely into a gel after a breakdown virtually coincided.

The last, not the least is an issue of temporal stability in the systems with nano-carbon. In first place we addressed it by monitoring optical absorption spectra. Fig. 2 exemplifies stability of materials: it gives spectral lines for a just-processed material (SWCNTs in 18 % wt. aqueous mixture of Pluronic) and the same sample stored in the fridge (5°C) in the liquid-phase state during 4 months and studied by spectroscopy at ambient temperature as the hydro-gel. All the characteristic peaks are sustained, a displacement of spectral lines did not surpass 5%. We also measured rheological polytherms in all of the samples, which were kept at ambient temperatures for a period of 4 months as well. As is seen in the Fig. 3 (b) by an example of a solution with 22 wt% of the polymer, principal features of the damping factor dependency vs.



**Fig. 6.** Hydro-gel (22% wt. Pluronic) with SWCNTs after optical breakdown (encircled) by high-power laser irradiation (left), and the same sample regenerated by temperature drop down to 5°C (duration 10 min) and subsequent gelation (right); in both cases pictures are taken at room temperature.

temperature were kept intact. After 20 months of storage solutions with polymer concentration of 18 wt% and above preserved homogeneity and complied with an inverted-tube test. Some of the samples with lower polymer concentrations, however, demonstrated a phase split on this time scale.

#### 4. Conclusions

Summing up, we state that doping of aqueous suspensions of SWCNTs and CB, stabilized by an amphiphilic polymer Pluronic F-127, by additional amounts of the latter provides transparent solid-like (viscosity spanning  $(2-3) \cdot 10^5$  mPa s) hydro-gels stable at room temperature on a time scale of several months. Limiting curves of the hydro-gel containing nano-carbon in relevant concentrations show up commensurable with those of aqueous suspensions regarding limiting thresholds and contrast. Programming of the phase state of the composite material can be done on the platform of the phase diagram of its water-polymer matrix. A salient peculiarity of the systems studied consists in a possibility of material regeneration in case of its disruption by high-intensity laser irradiation by thermo-reversible phase transition. Regularities observed can form a platform for the design of thermo-healing nano-structured high-power laser resistant optical materials in a solid-like or solid phase state.

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#### References

- [1] J. Wang, Y. Chen, R. Li, H. Dong, L. Zhang, M. Lotya, J.N. Coleman, W.J. Blau, Nonlinear optical properties of graphene and carbon nanotube composites, in: Siva Yellampalli (Ed.), Carbon Nanotubes - Synthesis, Characterization, Applications, inTech, 2011, pp. 397–424.
- [2] J. Wang, D. Früchtl, W.J. Blau, The importance of solvent properties for optical limiting of carbon nanotube dispersions, *Opt. Commun.* 283 (2010) 464–468.
- [3] A.Yu Vlasov, A.V. Venediktova, D.A. Videnichev, I.M. Kislyakov, E.D. Obratsova, E.P. Sokolova, Effects of antifreezes and bundled material on the stability and optical limiting in aqueous suspensions of carbon nanotubes, *Phys. Status Solidi B* 249 (2012) 2341–2344.
- [4] S. Dengler, C. Kübel, A. Schwenke, B. Eberle, Near- and off-resonant optical limiting properties of gold-silver alloy nanoparticles for intense nanosecond laser pulses, *J. Opt.* 14 (2012) 1–8 art. 075203.
- [5] S.A. Asher, S.-Y. Chang, A. Tse, L. Liu, G. Pan, Z. Wu, P. Li, Optically nonlinear crystalline colloidal self-assembled submicron periodic structures for optical limiters, *Mater. Res. Soc. Symp. Proc.* 374 (1995) 305–310.
- [6] C. Zheng, W. Chen, X. Ye, S. Cai, X. Xiao, M. Wang, Preparation and optical limiting properties of carbon nanotubes coated with Au nanoparticle composites embedded in silica gel-glass, *Mater. Lett.* 65 (2011) 150–152.
- [7] M. Pokrass, Z. Burshtein, G. Bar, R. Gvishi, Nonlinear optical and electrical conductivity properties of carbon nanotubes doped in sol-gel matrices, *SPIE Proc.* 9168 (2014) 1–7 art.916807.
- [8] Y. Lin, P. Alexandridis, Temperature-dependent adsorption of Pluronic F127 block copolymers onto carbon black particles dispersed in aqueous media, *J. Phys. Chem. B* 106 (2002) 10834–10844.
- [9] N.R. Arutyunyan, D.V. Baklashev, E.D. Obratsova, Suspensions of single-wall carbon nanotubes stabilized by pluronic for biomedical applications, *Eur. Phys. J. B* 75 (2010) 163–166.
- [10] E. Nativ-Roth, R. Shvartzman-Cohen, C. Bounioux, M. Florent, D. Zhang, I. Szeifer, R. Yerushalmi-Rozen, Physical adsorption of block copolymers to SWNT and MWNT: a nonwrapping mechanism, *Macromol* 40 (2007) 3676–3685.
- [11] M. Malmsten, B. Lindman, Effects of homopolymers on the Gel formation in aqueous block copolymer solutions, *Macromol* 26 (1993) 1282–1286.
- [12] R.K. Prud'homme, G. Wu, D.K. Schneider, Structure and reology studies of poly(oxyethylene-oxypropylene-oxyethylene) aqueous solution, *Langmuir* 12 (1996) 4651–4659.
- [13] G. Wanka, H. Hoffmann, W. Ulbricht, The aggregation behavior of poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene)-block-copolymers in aqueous solution, *Colloid Polym. Sci.* 268 (1990) 101–117.
- [14] P. Alexandridis, T.A. Hatton, Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer surfactants in aqueous solutions and at interfaces: thermodynamics, structure, dynamics, and modeling, *Colloids Surf., A Physicochem. Eng. Asp.* 96 (1995) 1–46.
- [15] G. Wanka, H. Hoffmann, W. Ulbricht, Phase diagram and aggregation behavior of poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) triblock copolymers in aqueous solutions, *Macromol* 27 (1994) 4145–4159.
- [16] I.R. Schmolka, A comparison of block copolymer surfactant gels, *J. Am. Chem. Soc.* 68 (1991) 206–209.
- [17] G.E. Yu, Y. Deng, S. Dalton, Q.-G. Wang, D. Attwood, C. Price, C. Booth, Micellisation and gelation of triblock copoly(oxyethylene/oxypropylene/oxyethylene), F127, *J. Chem. Soc. Faraday Trans.* 88 (17) (1992) 2537–2544.
- [18] E. Hecht, K. Mortensen, M. Gradzielski, H. Hoffmann, Interaction of ABA block copolymers with ionic surfactants: influence on micellization and gelation, *J. Phys. Chem.* 99 (1995) 4866–4874.
- [19] M. Malmsten, B. Lindman, Self-assembly in aqueous block copolymer solutions, *Macromol* 25 (1992) 5440–5445.
- [20] I.R. Schmolka, Preparation and properties of pluronic F-127 gels for treatment of burns, *J. Biomed. Mater. Res.* 6 (1972) 571–582.
- [21] H. Jiang, M. DeRosa, W. Su, M. Brabt, D. McLean, T. Bunning, Polymer host materials for optical limiting, *SPIE Proc.* 3472 (1998) 157–162.
- [22] B. Zhao, B. Cao, W. Zhou, D. Li, W. Zhao, Nonlinear optical transmission of nanographene and its composites, *J. Phys. Chem. C* 114 (2010) 12517–12523.
- [23] S. Luo, K. Chen, L. Cao, G. Liu, Q. He, G. Jin, D. Zeng, Y. Chen, Photochromic diarylethene for rewritable holographic data storage, *Opt. Express* 13 (2005) 3123–3128.
- [24] Q. Wang, G. Yu, Y. Deng, C. Price, C. Booth, Eluent gel permeation chromatography: application to the association of block copolymer F127 in aqueous solution, *Eur. Polym. J.* 29 (1993) 665–669.
- [25] A.V. Venediktova, V.N. Bocharov, A. Yu Vlasov, I.M. Kislyakov, V.M. Kiselev, E.A. Katz, E.D. Obratsova, A.S. Pozharov, S.A. Povarov, Aqueous suspensions of SingleWall carbon nanotubes: degree of aggregation into bundles and optical properties, *Opt. Spectrosc.* 116 (2014) 418–423.
- [26] K.J. McEwan, Paul A. Madden, Transient grating effects in absorbing colloidal suspensions, *J. Chem. Phys.* 97 (1992) 8748–8759.
- [27] D.O. Durand, V. Grolier-Mazza, R. Frey, Temporal and angular analysis of nonlinear scattering in carbon-black suspensions in water and ethanol, *J. Opt. Soc. Am. B* 16 (1999) 1431–1438.
- [28] S.M. Bachilo, M.S. Strano, C. Kittrell, R.H. Hauge, R.E. Smalley, R.B. Weisman, Structure-assigned optical spectra of single-walled carbon nanotubes, *Science* 298 (2002) 2361–2366.
- [29] A.V. Venediktova, A.Yu Vlasov, E.D. Obratsova, D.A. Videnichev, I.M. Kislyakov, E.P. Sokolova, Stability and optical limiting properties of a single wall carbon nanotubes dispersion in a binary water-glycerol solvent, *Appl. Phys. Lett.* 100 (2012) 1–5 art.251903.
- [30] B.K. Lau, Q. Wang, W. Sun, L. Li, Micellization to gelation of a triblock copolymer in water: thermoreversibility and scaling, *J. Polym. Sci. Part B Polym. Phys.* 42 (2004) 2014–2025.
- [31] N.A.K. Meznarich, B.J. Love, The kinetics of gel formation for PEO-PPO-PEO triblock copolymer solutions and the effects of added methylparaben, *Macromol* 44 (2011) 3548–3555.
- [32] L.C.P. Trong, M. Djaburov, A. Ponton, Mechanism of micellization and rheology of PEO-PPO-PEO triblock copolymers with various architectures, *J. Colloid Interf. Sci.* 328 (2008) 278–287.
- [33] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman spectroscopy of carbon nanotubes, *Phys. Rep.* 409 (2005) 47–99.
- [34] L. Vivien, D. Riehl, F. Hache, E. Anglaret, Nonlinear scattering origin in carbon nanotube suspensions, *J. Nonlinear. Opt. Phys. Mater.* 9 (2000) 297–307.
- [35] F.E. Hernández, W. Shensky III, I. Cohanoschi, D.J. Hagan, E.W. Van Stryland, Viscosity dependence of optical limiting in carbon black suspensions, *Appl. Opt.* 41 (2002) 1103–1107.
- [36] K. Mansour, M.J. Soileau, E.W. Van Stryland, Nonlinear optical properties of carbon-black suspensions (ink), *J. Opt. Soc. Am. B* 9 (1992) 1100–1109.