Crystalline polymer decoration on multiwalled carbon nanotubes: MWCNT-induced P4VP periodic crystallization in CO₂-expanded liquids

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Abstract. This work reports the functionalization of multi-walled carbon nanotubes (MWCNTs) with crystalline poly(4-vinylpyridine) (P4VP) in CO₂-expanded liquids (CXLs). The structure and morphology of MWCNT-induced polymer crystallization are examined, with the focus on molecular weight of P4VP (MW-P4VP), the pressure of CXLs and the concentration of P4VP. First, it is observed that the crystallization morphologies for the P4VP/MWCNTs composite with a low molecular weight P4VP (LMW-P4VP) matrix could be finely controlled in CXLs, and it is surprising to find that the P4VP₈₇₀₀ wrapping patterns undergo a morphological evolution from dot crystals to dotted helical wrappings, and then to dense helical patterns by facile pressure tuning under lower polymer concentration. In other words, the CXLs method enables superior control of the P4VP crystallization patternings on MWCNTs, particularly efficient for LMW-P4VP at lower polymer concentration. Meanwhile, the CXL-assisted P4VP crystal growth mechanism on MWCNT is investigated, and the dominating growth mechanism is attributed to ‘normal epitaxy’ at lower P4VP concentration rather than ‘soft epitaxy’ at higher concentration. We believe that this work reports a new crystalline polymer wrapping approach in CXLs to noncovalent engineering of MWCNTs surfaces.

Keywords: polymer composites, polymer crystallization, carbon nanotubes, poly(4-vinylpyridine), CO₂-expanded liquid

1. Introduction

Carbon nanotubes (CNTs) have attracted tremendous attention in recent years because of their superb optical, electronic and mechanical properties. However, the problem of poor solubility and processability remains a severe limitation to the extensive use of CNTs, which explains the continuous interest in a further functionalization and modification of the CNT surface. Both chemical functionalization and non-covalent wrapping methods have been reviewed recently [1, 2]. Herein, non-covalent functionalization of CNTs is of particular interest because it enables one to tailor their properties while still preserving nearly all of the nano-

tube’s intrinsic properties. The non-covalent methods involve using soft matter such as surfactants, oligomers, biomolecules and polymers to ‘wrap’ CNTs, to enhance their solubility or dispersibility [3–5].

Polymeric solubilization and functionalization of CNTs can play a vital role in exploring and developing its application. Polymer/CNT nanocomposite (PCN) is one of the most promising fields for CNTs [6, 7]. The potential applications of PCNs include conductivity enhancement, electrostatic dissipation and aerospace structural materials, and the properties of PCN usually differ substantially from those of the pristine polymer matrix, and a variety of

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polymers have been studied to form nanocomposites with CNTs depending on the targeted properties [1]. Recently, PCNs formed by CNTs and semicrystalline polymers such as isotactic polypropylene (iPP), polyethylene (PE), polyvinyl alcohol, polyacrylonitrile, poly(3-caprolactone), thermoplastic polyimide, conjugated organic polymer, as well as thermoplastic elastomers such as polyurethane systems have been studied [1, 8, 9]. Wrapping CNTs with crystalline polymers is thought to be an ideal functionalization method considering the excellent mechanical properties of crystalline polymers as well as the potential specific chain registry of different polymers upon CNTs. This method can retain the structural integrity of CNTs and simultaneously overcome the disability of the noncovalent modification method [8]. The CNT-induced polymer crystallization with the focus on the nanohybrid shish kebab (NHSK) structure have recently been reviewed by Li *et al.* [1].

Gas expanded liquids (GXLs) are mixtures consisting of a liquid organic solvent and a near-critical gas such as CO₂. These mixtures are currently being explored as potential replacements for pure organic solvents in chemical processing [10–12]. As such, they reflect a compromise between the use of conventional solvents, which are a major source of industrial pollution, and completely benign solvents like neat CO₂, whose poor solvent qualities and high pressure requirements have limited its application. In addition to the environmental benefits of GXLs, the ability to readily pressure tune the mole fraction of the gaseous component and thereby alter the solvating power, fluidity, and many other properties of these solvents proves advantageous in a variety of applications, such as materials processing [13, 14], analytical separations [15] and cleaning [16], and as media for organic reactions [11, 17, 18]. CO₂-expanded liquids (CXLs) are the most commonly used class of GXLs because of the safety and economic advantages of CO₂. CXLs have been regarded as the ideal solvents in a variety of roles including inducing separations, precipitating fine particles, and facilitating polymer processing [19]. CO₂ dissolution has been shown to lower the melting temperature, the crystallization temperature, and the glass transition temperature and to raise the rate and degree of crystallization for a variety of polymers, and polymer process in CXLs taking

advantage of the melting-point lowering and viscosity-lowering effects has been used to adjust particle size and morphology of polymers and to facilitate extrusion, foaming, impregnation, and mixing or co-molding of polymers [19]. Moreover, GXLs/CXLs combine the beneficial properties of compressed gases and of conventional solvents, leading to a new class of tunable solvents that are often the ideal type of solvents for a given application while simultaneously reducing the environmental burden through substantial replacement of organic solvents with environmentally benign CO₂ [19].

This work aims at reporting the functionalization of MWCNTs with polymers in CXLs, and the model polymer used is poly(4-vinylpyridine) (P4VP). P4VP is so intriguing material and there are several reasons for choosing it as our functional polymer. First of all, it has reactive pyridine group for coordinative with transition metals, which can be widely used in the field of catalysis [20–23], humidity sensitive material [24], waste water treatment [25, 26] and also as a host ligand of metal-containing chromophores [27, 28]. Moreover, its solution behavior can be changed significantly, being a hydrophobic polymer in apolar solvents and a cation polyelectrolyte in water at low pH [29, 30]. Therefore, the pH-sensitive P4VP can be readily quaternized by alkylgen and then form the positively charged polyelectrolytes as sensors and actuators [31, 32] and the N-alkylated pyridinium polymers as antimicrobial materials [33]. Thus, the unique hybrid structure of P4VP/MWCNT nanocomposite is expecting to play a vital role in exploring and developing the potential applications of the corresponding PCNs.

In this article, efforts are made to examine the structure and morphology of MWCNT-induced P4VP crystallization, with the focus on three types of peripheral effect on the periodic morphology change. We shall first discuss the effect of the molecular weight of P4VP, followed by the pressure of CXLs and the concentration of P4VP effect on the crystallization behavior. Meanwhile, the mechanism of CXL-assisted P4VP crystal growth on MWCNT is investigated. We believe that this work reports a new wrapping approach in CXLs to noncovalent engineering of MWCNTs surfaces that leads to an enhancement of solubility of MWCNTs and enables superior control of the relative placement of functionalities on the nanotube surface. The unique peri-

odic wrapping PCNs in CXLs can serve as a nano-scale template for CNT functionalization in a milder way compared to the well-known supercritical anti-solvent (SAS) processes.

Here, the difference between a CXL process and a SAS method should be mentioned. According to the phase behavior of the solvent mixture CO₂+dimethyl sulphoxide (DMSO) in this work, the SAS processes correspond to an operating region above the critical pressure of the mixture (P_c). At conditions above the P_c , DMSO and CO₂ are miscible in the whole composition range and polymer modification behavior results from gas-phase nucleation. The CXL processes are under conditions below the mixture critical pressure, and there exists a vapor-liquid equilibrium, and the CXL material processing is usually conducted in the liquid phase of the solvent mixture. In this work, the critical composition (critical mole fraction of CO₂, x_{C,CO_2}) and critical pressure of CO₂-DMSO at 338.2 K are $x_{C,CO_2} = 0.860$ and $P_c = 15.11$ MPa, respectively [34]. The experimental pressures are chosen to be lower than P_c and along the bubble-point curve at 338.2 K in CO₂-expanded DMSO. Therefore, the MWCNT functionalization in CXLs can be performed under milder operating conditions in contrast with the SAS processes.

2. Experimental section

2.1. Materials

MWCNTs were from Tsinghua University (China) with a purity of 93 wt%. Dimethyl sulphoxide (DMSO) and acetic anhydride (CH₃CO)₂O were supplied by the Damao Chemical Reagent Co., Ltd. (Tianjin, China). The monomer 4-vinyl pyridine (4VP) and Benzoyl Peroxide (BPO) were from Alfa Aesar (Beijing, China), and 2,2,6,6-tetramethyl-piperidine-N-oxyl (TEMPO) was supplied by Dengfeng Chemical Reagent Co., Ltd. (Tianjin, China). CO₂ with a purity of 99.95% was provided by Zhengzhou Shuangyang Gas Co. (China).

4VP was purified prior to use by fractionated distillation. BPO was purified by reprecipitation of a saturated dried chloroform solution by methanol. TEMPO and (CH₃CO)₂O were used as received.

P4VP₈₇₀₀ ($M_n = 8700$) and P4VP_{45 000} ($M_n = 45000$) used in this work were prepared in our lab. MWCNTs were dried in a vacuum oven at 308.2 K for 24 h before use.

2.2. Preparation of P4VP

P4VP₈₇₀₀ was prepared according to the literature [35], and P4VP_{45 000} prepared by a method described by Fischer [36]. In a typical polymerization procedure, a two-necked round-bottom flask was loaded with an appropriate amount of TEMPO, 4VP, BPO, and/or (CH₃CO)₂O; degassed by an argon gas purge; and sealed off under vacuum. The temperature of the polymerization and the duration was varied. P4VP formed, was end-capped with TEMPO, was precipitated in hexane, and dried under vacuum. The detailed reaction conditions for the preparation of P4VP, the number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of P4VP determined by Gel Permeation Chromatography (GPC) are provided in Table 1.

2.3. The functionalization of MWCNTs by P4VP

The experimental apparatus is illustrated in Figure 1. Typically, appropriate amount of P4VP were dissolved in an organic solvent DMSO at a suitable temperature. 0.1 mg of MWCNTs was dispersed in DMSO solution, the mixture was then ultrasonicated for 2–4 h at the temperature between 298.2–318.2 K in order to disperse the MWCNTs homogeneously in the solution. The dispersion was then added into P4VP/DMSO solution in a tube. After equilibration, the tube containing the mixture was quickly transferred into a stainless-steel autoclave at the temperature of 338.2 K. CO₂ was then charged into the autoclave to achieve the desired pressure

Table 1. Polymerization of 4-vinyl pyridine at different reaction conditions

Sample	Time [h]	Accelerator	Temperature [K]	TEMPO/BPO molar ratio	M_n^a	M_w/M_n^a
1	16	(CH ₃ CO) ₂ O ^b	368.2–408.2	1.30:1	8700	1.66
2	7	–	398.2	0.65:1	45000	1.88

^aNumber-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by Gel Permeation Chromatography (GPC) in DMF at 313.2 K, flow rate 1 ml/min

^b1% (w/w)

Figure 1. CXLs experimental apparatus description diagram: (1) temperature controller; (2) magnet; (3) magnetic stirrers; (4) syringe pump; (5) pump controller; (6) gas cylinder; (7) cooling jacket; (8) autoclave (9) pressure transducer; (10) thermoelectric couple; (11) heating-jacket; and (12) pressure indicator

within a short time. After 3 h reaction in CO₂-expanded DMSO, the system was slowly depressurized and the sample was collected and labeled. Comparative experiments of P4VP₈₇₀₀ or P4VP_{45 000} decorated MWCNTs under the same experimental conditions free of CO₂ were also performed, and the corresponding TEM images are provided in Figure 2.

2.4. Characterization methods

The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of P4VP were determined by GPC (1200 series, Agilent Technologies U.S.A.), and are tabulated in Table 1. The morphol-

ogy of P4VP functionalized MWCNTs was characterized by transmission electron microscopy (TEM). Samples were collected on a TEM grid and conducted using a JEOL JEM-2100 microscope with an accelerating voltage of 200 kV.

3. Results and discussion

The challenging task is to achieve the controlled functionalization of MWCNTs by adjusting the P4VP crystallization patternings. Accordingly, three types of peripheral effect such as MW-P4VP, the mass ratio of P4VP to MWCNT, and the pressure of CXLs on the periodic morphology change are examined. The experiments in this work are designed as such: MW-P4VP as M₈₇₀₀ and M_{45 000} are used, respectively; different mass ratio of P4VP to MWCNT as 5:1 (i.e., 0.01 wt% P4VP to 0.002 wt% MWCNTs) and 10:1 (i.e., 0.02 wt% P4VP to 0.002 wt% MWCNTs) are employed, respectively; and pressures are chosen along the bubble-point curve at 338.2 K in CO₂-expanded DMSO.

3.1. Effect of pressure in CO₂-expanded DMSO on the modification of MWCNTs with P4VP₈₇₀₀

The experimental conditions for the modification of MWCNTs are that reaction systems of P4VP concentration (0.01 wt%) and MWCNTs concentration (0.002 wt%) in DMSO were treated at 338.2 K and different pressures for 3 h, with pressures chosen to

A)

B)

Figure 2. TEM images of P4VP-decorated MWCNTs obtained in DMSO at 338.2 K for 3 h. The P4VP and MWCNTs concentrations in DMSO are 0.01 and 0.002 wt%, respectively: (A) P4VP₈₇₀₀; (B) P4VP_{45 000}.

be 6.22 MPa ($x_{\text{CO}_2} = 0.325$), 9.84 MPa ($x_{\text{CO}_2} = 0.505$) and 13.50 MPa ($x_{\text{CO}_2} = 0.715$), respectively, along the bubble-point curve at 338.2 K in CO_2 -expanded DMSO [34]. The compositions of the liquid phase (mole fraction of CO_2 , x_{CO_2}) were determined using known relations between the liquid composition and the coexisting vapor pressure of

CO_2 -DMSO phase diagram at 338.2 K [34]. The characteristic structures of P4VP_{8700} decorated MWCNTs are reflected in the TEM image (Figure 3A–3D). From Figure 3, it is obvious that P4VP_{8700} can grow by epitaxy on MWCNTs when MWCNTs are used as the modification subject. And it is interesting to find that multiple P4VP periodic

Figure 3. TEM images of P4VP_{8700} -decorated MWCNTs obtained in CO_2 -expanded DMSO conditions (338.2 K/varied pressure for 3 h) and P4VP_{8700} concentrations in DMSO (0.01 wt%), with MWCNTs concentrations of 0.002 wt%: (A)/(B) 6.22 MPa ($x_{\text{CO}_2} = 0.325$); (C) 9.84 MPa ($x_{\text{CO}_2} = 0.505$); (D) 13.5 MPa ($x_{\text{CO}_2} = 0.715$). The schematic representations of the helical structures of the $\text{P4VP}/\text{MWCNTs}$ composite are shown on image (C) and (D), respectively.

crystallization structures are formed with increasing pressure, i.e., the P4VP crystallization on MWCNTs undergoes a wrapping pattern transition first from dots (Figure 3A, 3B) to dotted-helix (Figure 3C), and then to a dense helical structure (Figure 3D) as the pressure increases from 6.22 to 9.84, and then to 13.50 MPa, respectively. So far as we know, it is the first time that the pressure dependence of morphological evolution of crystalline P4VP is obtained in GXLS.

The images from Figure 3A, 3B (6.22 MPa) indicate that the sidewalls of MWCNTs are decorated with some dots, and these dots are generally regarded as nanocrystals. The mechanism is suggested as follows. CO₂ cannot dissolve P4VP but is miscible with DMSO under suitable conditions. Therefore, compressed CO₂ is used as the antisolvent for P4VP/DMSO system. With the injection of CO₂ to the P4VP/DMSO system, the volume of the DMSO-rich phase is expanded owing to the dissolution of CO₂ and the solvent power on P4VP is reduced, therefore P4VP molecules precipitate out of the supersaturated solution and start to be adsorbed on the surface of MWCNTs. With the increasing amount of P4VP wrapping, P4VP molecules with folded-chains begin to align along MWCNTs as dots crystal so as to decrease the polymer surface energy, i.e., P4VP dot crystals are formed on MWCNTs because this structure is energetically favorable and a cooperative orientation between the polymer chains and MWCNT axes supports this crystallization pattern. So at lower pressure as 6.22 MPa, there spawned tiny size of heteronucleus dots of P4VP on the MWCNTs almost everywhere. These P4VP dot-like nanocrystals formed on the MWCNTs at lower pressure could also be regarded as a steady intermediate state, which could further form ordered patterning of nanohybrid structure when suitable experimental conditions are achieved. Upon increasing CO₂ pressure to 9.84 MPa, the solvent strength of the CXLs would further decrease due to more CO₂ dissolved in DMSO; therefore more P4VP can be deposited. Under such circumstance, there are two possible factors that affect the nanohybrid P4VP crystal growth: the epitaxial growth of P4VP on CNTs and geometric confinement [1]. Here, the size of P4VP₈₇₀₀ may be relatively small compared to the pristine MWCNTs (average diameter about 25–30 nm) used in the

work. Therefore, on the surface of the CNTs with a diameter larger than the polymer size, the polymer behaves as if it were on a flat surface. Strict lattice match and epitaxy are therefore the main growth mechanisms herein [1]. And because of the different rolling directions or chiralities of the CNTs, there exist multiple orientations of the graphitic lattice with respect to the CNT axis. Meanwhile, polymer chains normally possess a coil conformation [37], thus, with more P4VP deposited under higher pressures (9.84 and 13.50 MPa), multiple orientations of the P4VP molecules would coil along the MWCNT axis with crystal lamellae oblique to the MWCNT axis and finally a helical P4VP wrapping pattern is formed owing to the dominance of the epitaxy factor. With CO₂ pressure further increases up to 13.50 MPa, more P4VP can be deposited compared to that at 9.84 MPa, therefore a denser P4VP helix on MWCNTs at 13.50 MPa is obtained whereas a dotted helical wrapping of P4VP is formed at 9.84 MPa.

3.2. Modification of MWCNTs with P4VP_{45 000} in CO₂-expanded DMSO

The experimental conditions are that the P4VP_{45 000} (concentration 0.01 wt%) and MWCNTs (concentration 0.002 wt%) in DMSO were treated at 338.2 K and different pressures for 3 h, with pressures chosen to be 10.47 MPa ($x_{\text{CO}_2} = 0.539$) and 11.84 MPa ($x_{\text{CO}_2} = 0.617$), respectively, along the bubble-point curve at 338.2 K in CO₂-DMSO [34]. The structures of P4VP_{45 000} decorated MWCNTs are shown in the TEM image (Figure 4A–4D).

It is shown from Figure 4 that the P4VP₄₅₀₀₀ crystallization on MWCNTs undergoes a wrapping pattern evolution from dots (Figure 4A, 4B) to multi-helical wrapping (Figure 4C, 4D) as the pressure increases from 10.47 to 11.84 MPa, which somewhat resembles the crystallization morphological transition reflected in P4VP₈₇₀₀/MWCNTs composite series with the difference in the helical wrapping patterns at higher pressures. At higher pressures, single helical wrappings of P4VP₈₇₀₀ are formed on MWCNTs whereas a multi-helical P4VP₄₅₀₀₀ structures are produced for P4VP_{45 000}/MWCNTs composite.

The reasons for the multi-helical P4VP_{45 000} structures are possibly as follows. It is easy to understand that the polymer chain is longer for P4VP₄₅₀₀₀

Figure 4. TEM images of P4VP₄₅₀₀₀-decorated MWCNTs obtained in CO₂-expanded DMSO conditions (338.2 K/ varied pressure for 3 h) and P4VP_{45 000} concentrations in DMSO (0.01 wt%), with MWCNTs concentrations of 0.002 wt%: (A)/(B) 10.47 MPa ($x_{\text{CO}_2} = 0.539$), (B) is the enlarged image of (A), (C)/(D) 11.84 MPa ($x_{\text{CO}_2} = 0.617$)

than that for P4VP₈₇₀₀, thus both the solubility and the molecular mobility in DMSO are poorer for P4VP_{45 000} compared to P4VP₈₇₀₀. It is generally believed that the amount of P4VP precipitation and the consequent number of nucleation are greatly increased with increasing pressure of CO₂ in P4VP_{45 000}/MWCNTs system, so it is reasonable that multiple strands of the P4VP_{45 000} would coil around the MWCNTs and a multi-helical P4VP_{45 000} structures formed on MWCNTs rather than a simple

helical crystallization for low molecular weight molecules as P4VP₈₇₀₀.

3.3. Effect of P4VP Concentration on the modification of MWCNTs – polymer concentration dependence of crystal growth mechanism

From the aforementioned modification results using different MW-P4VPs under the same P4VP concentration, it seems that the wrapping morphologies for

the P4VP/MWCNTs composite with a LMW-P4VP matrix could be finely regulated in CXLs. So, in this section, the LMW-P4VP (i.e., P4VP₈₇₀₀) is chosen to investigate the potential P4VP concentration dependence of MWCNTs modification.

The experimental conditions with higher P4VP concentration are that the P4VP₈₇₀₀ (concentration

0.02 wt%) and MWCNTs (concentration 0.002 wt%) in DMSO were treated at 338.2 K and different pressures for 3 h, with pressures chosen to be 7.80 MPa ($x_{\text{CO}_2} = 0.400$), 9.31 MPa ($x_{\text{CO}_2} = 0.477$) and 11.58 MPa ($x_{\text{CO}_2} = 0.602$), respectively, along the bubble-point curve at 338.2 K in CO₂-DMSO [34]. The corresponding structures of P4VP₈₇₀₀/

Figure 5. TEM images of P4VP₈₇₀₀-decorated MWCNTs obtained in CO₂-expanded DMSO conditions (338.2 K/ varied pressure for 3 h) and P4VP₈₇₀₀ concentrations in DMSO (0.02 wt%), with MWCNTs concentrations of 0.002 wt%: (A) 7.80 MPa ($x_{\text{CO}_2} = 0.400$); (B) is the enlarged section of (A); (C) 9.31 MPa ($x_{\text{CO}_2} = 0.477$); (D) 11.58 MPa ($x_{\text{CO}_2} = 0.602$). There are schematic representations of the P4VP/MWCNTs NHSK structure on image (A) and (D), respectively, P4VP form kebab crystals on MWCNT surface with polymer chains parallel to the MWCNT axis.

MWCNTs at higher polymer concentration (P4VP₈₇₀₀ 0.02 wt%) are shown in Figure 5A–5D, while the TEM images at lower polymer concentration (P4VP₈₇₀₀ 0.01 wt%) are shown in Figure 3A–3D. A nanohybrid shish-kebab (NHSK) like structure is observed from Figure 5: the central shish is MWCNTs, along the MWCNTs stems, round-shaped P4VP crystal kebabs can be regarded as periodically perpendicular to the stem axis. Typical NHSK structures have been observed in a number of labs [8, 9, 38]. The variation trend for the size of the kebab is indicated in Table 2: with the increase in pressure, it is found that while the size of the kebab increases, the periodicity of the kebab decreases. Actually, it can be seen from Table 2 that although a change in pressure can help adjust the modification of MWCNTs to some extent, the pressure effect is not so remarkable. In other words, although the P4VP wrapping degree on MWCNTs increases with increasing pressure, the pressure-dependent decoration effect is less notable at higher P4VP concentration.

The NHSK-like structure would suggest its formation mechanism. The orthogonal orientation between kebab surface and the MWCNT axis indicates that P4VP chains are parallel to the MWCNT axis. As mentioned previously, the epitaxial growth of P4VP on MWCNT and geometric confinement are two possible factors that affect NHSK growth. If the epitaxy factor dominates for all the MWCNTs, multiple orientation of the P4VP crystal lamellae should be observed, which is not supported by our results, indicating that ‘soft epitaxy or geometric confinement’ factor may predominate the NHSK formation, wherein strict lattice matching is not demanded while a cooperative orientation between the polymer chains and the MWCNT axes is required. Thus, when P4VP₈₇₀₀ with higher polymer concentration starts to crystallize onto the surface of MWCNTs, geometric confinement is the major factor and the polymer chains are exclusively parallel to the

MWCNT axis, disregarding the MWCNT chirality, and then the shish-kebab-like structures are formed herein [1].

People may wonder why the NHSK-like structures (Figure 5, P4VP₈₇₀₀ concentration 0.02 wt%) instead of the helical morphology (Figure 3, P4VP₈₇₀₀ 0.01 wt%) are formed in P4VP₈₇₀₀/MWCNTs composite under higher P4VP concentration? It is suggested that the chain mobility (or molecular mobility) could also be vital in the formation of oriented crystal structure [39]. The P4VP concentration dependence of the formation of NHSK can be discussed on the basis of the chain mobility. Provided the same MW-P4VP and similar CXL conditions, in systems with higher P4VP concentration, the P4VP chain mobility should be weaker than that under lower P4VP concentration. It is predicted that under higher P4VP concentration with poorer polymer mobility, the P4VP chains prefer to be ‘folded coiling’ conformation rather than ‘elongated coiling’ conformation under lower concentration. That is, the ‘folded coiling’ P4VP chains prefer to soft-epitaxially grow into the kebabs (with kebab lamellae perpendicular to the MWCNT axis) under less mobile polymer conditions while the long coiled chains can be easily stretched to form helical wrappings with polymer chains oblique to the MWCNT-axis under lower polymer concentration. In other words, the evolution of the shish-kebab structure could be explained as the coil-stretch theory [39]. The helical wrapping forms when the polymer chains undergo a transition from a coiled conformation to a highly elongated state.

As to the variation trend for the size of the kebabs with pressure: with the pressure of CO₂ kept increasing, the amount and speed of CO₂ dissolved in DMSO increase and the solvent strength of DMSO becomes weaker; thus both the amount and the speed of P4VP precipitation can be greatly increased, and can induce the increase of the nucle-

Table 2. Size of the kebabs in the P4VP₈₇₀₀/MWCNTs NHSK structure produced with the P4VP₈₇₀₀ (concentration 0.02 wt%) and MWCNTs (concentration 0.002 wt%) in CO₂-expanded DMSO at 338.2 K and different pressures: (A) and (B) 7.80 MPa ($x_{\text{CO}_2} = 0.400$); (C) 9.31 MPa ($x_{\text{CO}_2} = 0.477$); (D) 11.58 MPa ($x_{\text{CO}_2} = 0.602$)

Sample	Pressure [MPa]	Lateral size of the kebabs [nm]	Thickness of the kebabs [nm]	Periodicity of the kebabs [nm] ^a
A and B	7.80	25–40	30–50	20–50
C	9.31	30–45	20–35	~0
D	11.58	40–50	20–30	~0

^aPeriodicity is defined as the distance between the adjacent kebab centers

Figure 6. P4VP Crystallization on MWCNTs in CO₂-expanded liquids

ation number, which can lead to the formation of more kebabs. Therefore, both the size and the number of the kebabs would increase.

The suggested formation procedure is illustrated in Figure 6, which includes the initial nucleus and crystal growth to form helical or kebab structure in the later period.

3.4. The enhancement of MWCNTs dispersibility in DMSO

A photograph of samples dispersed in DMSO is shown in Figure 7. The three vials on the left contained MWCNTs (0.002 wt %) in DMSO, and the right three ones contained the samples of P4VP₈₇₀₀ modified MWCNTs, with P4VP₈₇₀₀ (0.02 wt%) and MWCNTs (0.002 wt%) in DMSO after reaction at 11.58 MPa ($x_{\text{CO}_2} = 0.602$) and 338.2 K for 3 h. From the images in Figure 7, we can observe that the MWCNTs precipitate easily in DMSO. The MWCNTs cannot disperse well in DMSO and start partially precipitating just 30 min after the ultrasonication (Figure 7B), whereas there is no obvious

Figure 7. The three vials on the left contained MWCNTs (0.002 wt%) in DMSO. The right three ones contained P4VP₈₇₀₀ modified MWCNTs in DMSO, with P4VP₈₇₀₀ (0.02 wt%) and MWCNTs (0.002 wt%) in DMSO after reaction at 11.58 MPa ($x_{\text{CO}_2} = 0.602$) and 338.2 K for 3 h. First, all the samples were placed in the vials and ultrasonicated for 30 minutes, and the photographs were taken after the post-treatments on the samples as follows. (A) right after the ultrasonication; (B) 30 minutes after the ultrasonication; (C) 1 hour after the ultrasonication; (D) right after the ultrasonication; (E) after rotation at 4000 rpm for 5 minutes; (F) after rotation at 4000 rpm for 10 minutes.

aggregation in the P4VP modified MWCNTs under rotation at 4000 rpm for 10 minutes (Figure 7F). Obviously, the modified MWCNTs disperse well in DMSO. Here the solutions (Figures 7E, 7F) represent a good dispersion of MWCNTs/P4VP to form a stable system.

4. Conclusions

In conclusion, wrapping MWCNTs with amphiprotic polymer P4VP in CO₂ expanded DMSO was carried out. Firstly, about the pressure dependence of the MWCNTs modification: at lower polymer concentration (P4VP₈₇₀₀ 0.01 wt%), the pressure of CXLs has a significant influence on the modification morphology. The morphological evolution of crystalline polymer on MWCNTs can be easily achieved by facile pressure tuning, wherein a structural evolution in P4VP₈₇₀₀/MWCNTs composites was observed from dots to dotted helix, and then to dense helix; while at higher polymer concentration (P4VP₈₇₀₀ 0.02 wt%), a NHSK-like structures rather than helical wrappings are obtained, the corresponding composite structure is only slightly pressure dependent; a less notable pressure dependence is also observed for P4VP₄₅₀₀₀/MWCNTs, wherein a structural transition from dots to multi-helix was achieved with increasing pressure. Secondly, about the polymer concentration dependence of crystal growth mechanism: under higher polymer concentration (P4VP₈₇₀₀ 0.02 wt%), the same MW-P4VP has different packing styles on the surface of MWCNTs and thus different crystal morphologies. The dominating crystal growth mechanism is attributed to ‘soft epitaxy’ at higher P4VP concentration rather than ‘normal epitaxy’ at lower concentration. Finally, comparative experiments of P4VP₈₇₀₀ or P4VP_{45 000} decorated MWCNTs under the same experimental conditions free of CO₂ were also performed (the results are provided in Figure 2). From Figure 2, the wrapping pattern of P4VP on MWCNTs (in DMSO without CO₂) is found to be a simple coating style with film thickness about 1–2 nm and around 1–6 nm for P4VP₈₇₀₀ and P4VP_{45 000}, respectively. So, it is undoubtedly that the CXL method offers superior control of the P4VP crystallization patterns on MWCNTs in contrast with the conventional way.

We believe that the molecular weight, the concentration of P4VP as well as the pressure in GXLs are

effective approaches to control the polymer crystallization structures on MWCNTs. The combination of desired pressure of CO₂ and MW-P4VP helps to modify the MWCNTs in a controllable way at suitable polymer concentration and temperature, which could serve as a model process to achieve ideal polymer crystals for structural and morphological study. Meanwhile, this work offers a new polymer wrapping approach in CXLs to noncovalent engineering of CNTs surfaces that leads to an enhancement of solubility or dispersibility of CNTs and enables superior control of the relative placement of functionalities on the CNT surface. The unique hybrid structure of P4VP/MWCNT nanocomposites would play a vital role in exploring and developing the potential applications of the corresponding PCNs.

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