

Formation Mechanism of β -Phase in PVDF/CNT Composite Prepared by the Sonication Method

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Received August 7, 2009; Revised Manuscript Received October 1, 2009

ABSTRACT: Two poly(vinylidene fluoride)(PVDF)/carbon nanotube (CNT) composites are prepared by solution sonication and mechanical mixture approaches. It is found that α -phase coexists with β -phase in the composite prepared by sonicating the PVDF/CNT mixture solution, while no β -phase can be observed in the composite prepared from the mechanical mixture route. With the help of the density functional theory calculations, it is explained that a large amount of energy is required for transforming trans–gauche–trans–gauche' (TGTG') into trans–trans (TT) conformations and the TT molecular chain can be bound on the CNT surface tightly. The emergence of β -phases is independent of zigzag carbon atoms on the CNT surface. The formation mechanism of β -phase is proposed based on the theoretical calculations and experimental results.

Introduction

Poly(vinylidene fluoride) (PVDF) is a particularly interesting and attractive polymer material because of its high piezoelectricity.¹ PVDF exhibits at least four crystalline forms, i.e. α -, β -, γ -, and δ -phases. Among the four polymorphs, the α -phase is the most common and stable polymorph, while the β -phase is the most important one due to its piezoelectric and pyroelectric properties and exhibits outstanding performance when used in practical devices. The β -phase may be obtained by drawing films containing α -phase,² by applying an extremely high electric field to the α -phase of PVDF,³ by crystallization from solution under special conditions,⁴ or by crystallization from the melt.⁵ Incorporation of organically modified clay in PVDF also results in the β -phase of PVDF.^{6,7} Levi et al. also observed that the addition of carbon nanotubes (CNTs) led to β -phase of PVDF by sonication.⁸ A possible explanation was proposed by Manna et al.⁹ They assumed that the CNT surface has zigzag carbon atoms, which match with the all-trans conformation of β PVDF and as a result may induce crystallization of PVDF in the β -polymorphic structure. For the exact origin on the β -phase formation, however, there have been no extensive theoretical studies reported, especially in comparison with actual experimental observations so far.

In this paper, two PVDF/CNT composites are prepared by solution sonication and unsonication approaches. The PVDF/CNT composites are measured with X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. It is found that α -phase coexists with β -phase in the composite prepared by sonicating the PVDF/CNT mixture solution while for the composite prepared by the mechanical mixture there only exists α -phase PVDF crystals. It is explained by a very large energy barrier between trans–gauche–trans–gauche' (TGTG') and trans–trans (TT) conformations of PVDF molecule. In addition, they all can be absorbed easily on the CNT surface and act as nucleating agents. A possible mechanism is proposed for β -phase formation in the PVDF/CNT composite prepared by sonication.

Experimental Section

PVDF powder used in this study is a product of Solvay Solexis from Belgium. The multiwalled CNTs, having a diameter in the range of 10–50 nm and a length ranging from 4 to 10 μ m, were grown via the chemical vapor deposition and were kindly provided by Shenzhen Dynanonic Co. Ltd., China. PVDF was dissolved in dimethylacetamide (DMAc), and the CNTs were dispersed in DMAc by sonication for 40 min. The PVDF solution was mixed with the CNT solution. The PVDF/CNT mixture solution was mechanically stirred at room temperature for 1 h and then was sonicated for 40 min before being poured into uncovered glass dishes, which were gently heated at 50 °C for 2 days for removing DMAc. Further drying of the mixture took place in a vacuum oven at 80 °C. In order to understand the effect of sonication on the crystalline structure of PVDF, a composite obtained from unsonicated PVDF/CNT mixture solution (i.e., mechanical mixture solution) was also prepared with the same method. The two composites reported here are 2 wt % CNTs. X-ray diffraction patterns were obtained with a Rigaku D/MAX-rA diffractometer with a rotating anode (Cu K α radiation, $\lambda = 0.51418$ nm) under a voltage of 40 kV and a current of 100 mA. Fourier transform infrared spectra were recorded on a Nicolet-DX FTIR spectrometer.

XRD patterns of the composites prepared by sonicating and unsonicated PVDF/CNT mixture solution are shown in Figure 1a. The peaks at 2θ values of 18.4°, 20°, and 26.5° can be assigned to the (100), (110), and (021) reflections of the α -phase of PVDF.^{10,11} If the PVDF/CNT mixture solution is sonicated during composite preparation, a new crystalline peak can be observed at $2\theta = 20.6^\circ$, which can be assigned to the (110) and (200) reflections of β -phase PVDF.^{10,11} FTIR spectra of the composites are shown in Figure 1b. The corresponding IR absorption band characteristics of α -phase are 530, 615, 765, 795, and 975 cm^{-1} , whereas for β -phase peaks in IR spectra are located at 510 and 840 cm^{-1} .^{7,12} For the composite prepared by sonicated PVDF/CNT mixture solution, two distinct absorption peaks of β -phase are observed at 510 and 840 cm^{-1} . These results along with XRD data clearly indicate that α -phase coexists with β -phase in the composite prepared by sonicated PVDF/CNT mixture solution, while only α -phase is presented in the composite coming from unsonicated mixture solution.

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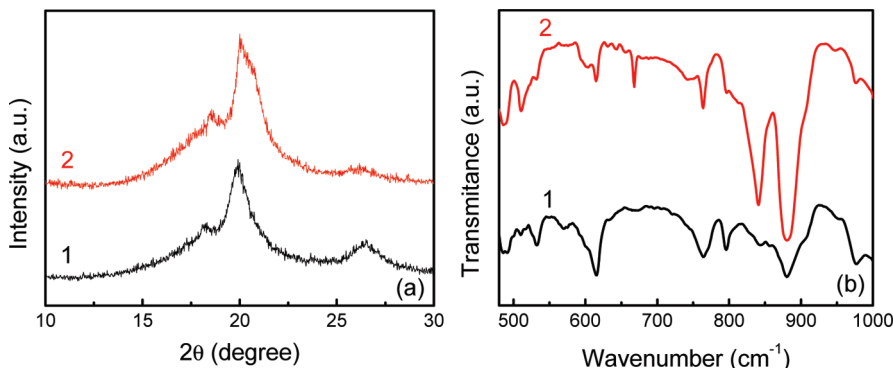


Figure 1. (a) XRD patterns of the composites prepared by (1) unsonicated and (2) sonicated PVDF/CNT mixture solution. (b) FTIR spectra of the composites prepared by (1) unsonicated and (2) sonicated PVDF/CNT mixture solution.

A previous research showed that sonication could lead to the formation of cross-linked polystyrene/CNT composite.¹³ In order to ascertain whether there is a cross-linking structure in the PVDF/CNT composite prepared by sonication, the solution extraction was carried out by refluxing the samples (250 mg) for 40 h in DMAc. The gel content was determined by

$$g = \frac{W_0 - W_1}{W_0} \times 100\%$$

where g is the gel fraction, W_1 is the weight of the sample after refluxing, and W_0 is the weight of the sample before refluxing. The obtained results showed that $g = 0$ for the sample prepared by sonication. It is evident that there is no chemical cross-linking in the PVDF/CNT composite after ultrasonic treatment.

Theoretical Calculations

In order to understand the observed spectra in more detail, we have performed the theoretical calculations using density functional theory (DFT). We have used the code DMOL3 available from Accelrys Inc.^{14,15} All-electron calculations were performed with a double numeric plus polarization basis set. For the exchange and correlation term, the local density approximation (LDA) was used as proposed by Perdew and Wang.¹⁶ It is well-known that the standard DFT could not properly treat the long-term dispersion interactions in which electronic overlap is very small,^{17,18} wherein LDA has a tendency to overestimate the binding energy, compared with experimental results. However, in our work, for physisorption, the adsorption energies are only used to compare the different geometries and to find the most favorable physisorption configuration of the PVDF molecular chains for which we need only relative values.

The α - and β -phases of PVDF are constructed with the TGTG' and TT molecular conformations, respectively, and two different conformations are shown in Figure 2. Because of our computation limitation, we only consider a segment of PVDF which consists of eight carbon atoms in the backbone and single-walled CNT. One-dimensional periodic boundary condition was applied along the tube axis, in which periodically repeating tetragonal supercells in which individual tube was separated by a vacuum region. In the adopted vacuum region, the intervals among the tube were kept as 50 Å. These intervals were large enough to ensure negligible interaction between the tube and its periodic images. The zigzag tube (10, 0) per four units and armchair tube (5, 5) per seven units were chosen.

First of all, we will estimate whether the molecular chains with TT and TGTG' configurations can be adsorbed on the CNT surface. We consider two configurations of the binding of PVDF molecular chains on the CNT surface. One is that H atoms and CNT surface are face-to-face, as shown in Figure 3a,c,e,g.

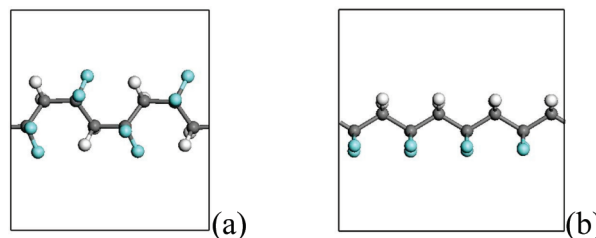


Figure 2. (a) TGTG' and (b) TT type chains of PVDF, where the white and cyanine balls denote the hydrogen and fluoride atoms and the gray balls represent carbon atoms.

Another is that F atoms and CNT surface are face to face, as shown in Figure 3b,d,f,h. Because the adsorption energies of other configurations will be between above two configurations, other configurations are not considered. Their corresponding adsorption energies are calculated to determine the most energy-favorable configuration, as listed in Table 1. It is found that the TT molecular chain prefers to be absorbed on the CNT surface compared with TGTG' molecular chain, and the configuration in which H atoms and CNT surface are face-to-face are more stable than that where F atoms and CNT surface are face-to-face. The electronegativity value of C atom is between H atom and F atom. Hence, in the PVDF, the negative charge transfer from H to C atom and the negative charge is accumulated around the F atoms. The interaction between the H atom with positive charge in PVDF and C atom with π orbital in CNT is stronger than that between the F atom with negative charge and C atom with π orbital. In addition, it is noted that the different adsorption energies between zigzag and armchair CNTs are very small. It indicates that the adsorption energy of PVDF on the CNT surface is independent of chirality of CNT. Although the adsorption energies are not large, it is possible to increase the binding of PVDF on the functionalized CNT.¹⁹

PVDF molecular chains can exhibit TGTG' or TT conformations which all can be adsorbed on the surface of CNTs, which indicate that there will be barriers between them. To evaluate these barriers, a linear synchronous transit method is used, as shown in Figure 4. The configurations of PVDF-adsorbed CNT, in which H atoms and CNT surface are face-to-face, are marked by C (TGTG') and D (TT). A and B denote the configurations in which TGTG' or TT molecular chains are far away from CNT, and the distance between them is about 21.0 Å (see Supporting Information for details). This interval is large enough to ensure that interaction between the tube and PVDF molecular chain is very weak. In our calculations, the energy to bind TGTG' or TT molecular chains on the CNT surface requires 0.30, 0.37 eV for the (5, 5) tube and 0.23, 0.39 eV for the (10, 0) tube, viz., from A to C and from B to D. It should be pointed out that we adopt

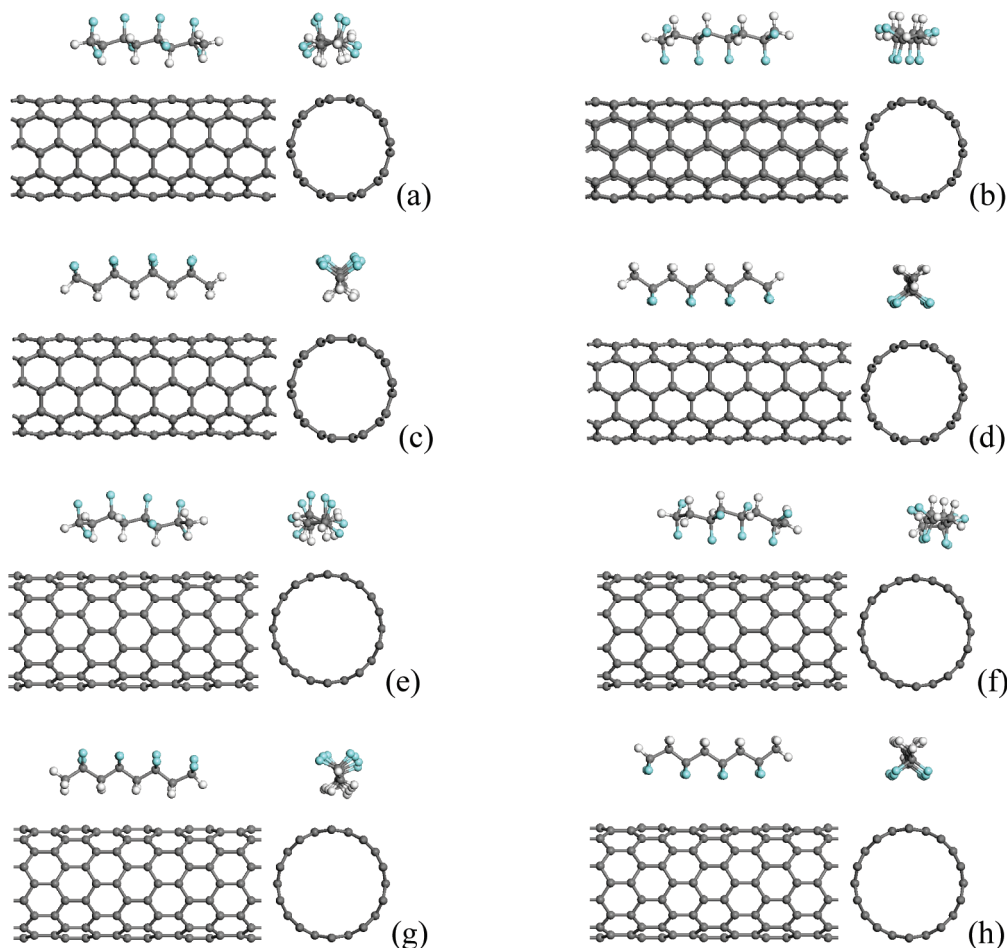


Figure 3. (a, b) TGTG' and (c, d) TT molecular chains of PVDF are absorbed on the armchair tube (5, 5), (e, f) TGTG', and (g, h) TT of PVDF are absorbed on the zigzag tube (10, 0). The molecular chain of PVDF consists of eight carbon atoms in the backbone.

Table 1. Adsorption Energies (eV) for the CNT with PVDF in Figure 3^a

type	TGTG'-1	TGTG'-2	TT-1	TT-2
(5, 5)	-0.64	-0.47	-0.94	-0.63
(10, 0)	-0.62	-0.46	-0.96	-0.51

^a TGTG'-1 and TT-1 denote that H atoms and CNT surface are face-to-face, and TGTG'-2 and TT-2 denote that F atoms and CNT surface are face to face. The molecular chain of PVDF is composed with eight carbon atoms in the backbone.

LDA scheme which has a tendency to overestimate the binding energy. Consequently, these energy barriers are small and may be overcome in ambient conditions. However, the energy barriers from C to D and from A to B are very high. It indicates that the formation of TT chain is unlikely at moderate condition and requires a large amount of energy from TGTG' to TT. In addition, it is also observed that TT-absorbed CNT is stable because the energy barriers from D to B and from D to C are very high. As shown in Figure 4, when TGTG' molecular chain is absorbed on the CNT, it is very difficult that TGTG' molecular chain can directly be transformed to TT molecular chain, viz., from C to D, which require 2.33 eV for (5, 5) and 1.81 eV for (10, 0) tubes. Hence, for the transition from TGTG' conformation to TT conformation, the route from A to B to D is likely.

Discussion

Although the TT molecular chain of PVDF prefers to be absorbed on the CNT surface in comparison with TGTG'

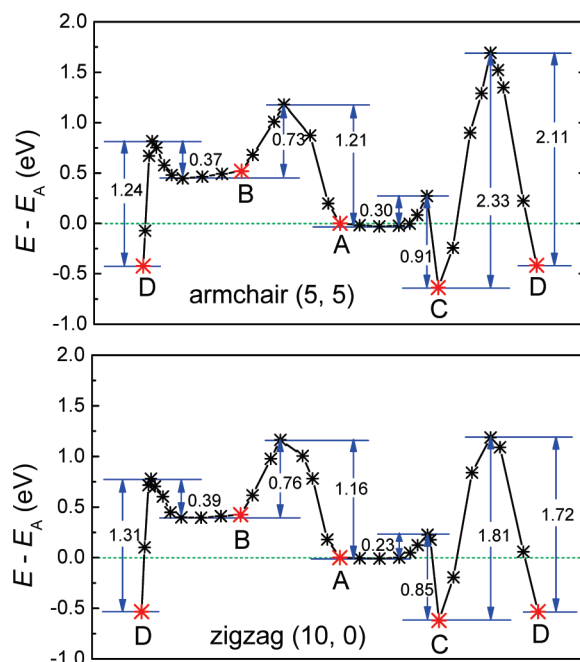


Figure 4. Relative energy versus the reaction path. A and B denote configurations that TGTG' and TT molecular chains are far away from CNT. C and D denote configurations that TGTG' and TT molecular chains are absorbed on the CNT surface. The unit of energy barrier is in eV.

molecular chain in Table 1, Hasegawa et al.²⁰ have shown that the energy of TT is higher than that of TGTG' chain of PVDF, and then the TGTG' conformation is more stable than the TT type which is also demonstrated by our calculations in Figure 4; viz., the relative energy of A is lower than that of B. Only through the special treatment,^{2-9,21} the stable TT chain can be obtained from TGTG' chain and then directly forms β -phase. Therefore, it is expected that there only exist TGTG'-type polymer chains in the unsonicated PVDF/CNT mixture solution. These polymer chains will be adsorbed on the surfaces of CNTs and form α -phase during crystallization, which is agreement with our XRD and FTIR results. However, for the sonicated PVDF/CNT mixture solution, there is reason to believe that some TGTG'-type polymer chains may be transformed into TT type by sonication. It is well-known that the effects of solution sonication on polymers can be both physical and chemical. Doktycz et al.²² reported that ultrasonic cavitation can generate a local temperature as high as 5000 K, local pressure as high as 50.6 MPa, and heating and cooling rate greater than 10^9 K/s. Under such conditions, PVDF chains are subjected to extremely large forces in the rapid liquid flows near collapsing cavitation bubbles and in the shock waves generated after bubble implosion. In this process, some TGTG' chains will obtain energy from the sonicating solution. Since there is no chemical cross-linking of PVDF/CNT composite prepared by solution sonication, these TGTG'-type molecular chains with high energy can easily overcome the energy barrier between TGTG' and TT configurations, viz., from A to B in Figure 4, and then can be transformed into TT-type chains. The TT-type molecular chains will be adsorbed on the surface of CNTs and act as nucleating agents of β -phases. In addition, it can be seen from Figure 4 that the energy barriers from D to B or from D to C are very high. Therefore, it is unfavorable for transforming TT conformation to TGTG' type, and TT molecular chains can be bound on the CNT surface tightly owing to a strong confining effect of CNTs.

In our previous work,²³ we found that CNTs can be wrapped by PVDF and form spherical particles with a diameter of several micrometers after sonicating PVDF/CNT mixture solution. For only PVDF prepared under the same sonication conditions, however, no spherical particles can be observed in the PVDF sample. It is concluded that CNTs are responsible for the formation of the spherical particles. On the basis of these experimental evidence, the growth process of β -phase may be explained as follows. There exist TGTG' and TT-type molecular chains in PVDF/CNT solution during sonication treatment. The adsorption energies in Table 1 indicate that these molecular chains can be adsorbed on the CNTs surface and then forming TGTG'/CNT and TT/CNT microparticles which can act as "seeds" in the crystallization process. When cavitation bubbles collapse during sonication process, a lot of TGTG' molecular chains near the bubbles acquire energy and are transformed into TT chains, and then these TT chains can be jetted to TT/CNT microparticles by the shock waves generated after bubble implosion, which leads to the growth of the TT/CNT microparticles. These particles with TT molecular chains will form β -phases during crystallization process. For the TGTG' molecular chains which are far away from the microbubbles, however, less energy can be acquired from the solution. Under such circumstance, TGTG' chains cannot be transformed into TT chains. These TGTG' chains will combine with the TGTG'/CNT particles in the flowing liquid and lead to forming α -phases during crystallization process. The growth rates of the two types of crystals are assumed to be same during crystallization of PVDF, which will result in α -phase coexisting with β -phase for the composite prepared by the sonicated mixture solution.

Conclusions

Two PVDF/CNT composites are prepared by solution sonication and mechanical mixture approaches. There only exists α -phase in the composite prepared by the unsonicated mixture solution while for the composite prepared by the sonicated mixture solution α -phase coexists with β -phase. With the help of the density functional theory calculations, it is predicated that both TGTG' and TT chains are able to be adsorbed on the CNT surface, and the TT molecular chain is bound on the CNT surface more tightly than the TGTG' molecular chain does. Because of sonication, some TGTG'-type polymer chains can be transformed into TT-type chains in the mixture solution. The TT-type molecular chains adsorbed on the CNTs surface can act as nucleating agents owing to a strong confining effect of CNTs, which result in the formation of β -phase during the crystallization of PVDF. The theoretical prediction is well in agreement with experimental observation.

Acknowledgment. The support from National Natural Science Foundation of China (Grants 50525204, 50832001, and 50902057), the special Ph.D. program (Grant 200801830025) from Ministry of Education, Science and Technology Development Programmer of Jilin Province (Grant 20090703), and the "211" and "985" project of Jilin University, China, is highly appreciated.

Supporting Information Available: TGTG' (A) and TT (B) molecular chains are far away from CNT surface, in which the distance between them is about 21.0 Å; TGTG' (C) and TT (D) molecular chains are adsorbed on the CNT surface, in which H atoms and CNT surface are face-to-face. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Fukada, E.; Tasaka, S.; Nalwa, H. *Ferroelectric Polymers*; Nalwa, H., Ed.; Marcel Dekker: New York, 1995; p 353.
- (2) David, L.; Winsor, J. I.; Scheinbeim, B. A. Effects of plasticizer on the mechanical and ferroelectric properties of uniaxially oriented β -phase PVDF. *J. Polym. Sci., Part B* **1996**, *34*, 2967.
- (3) Scheinbeim, J.; Nakafuku, C.; Newman, B. A.; Pae, K. D. High-pressure crystallization of poly(vinylidene fluoride). *J. Appl. Phys.* **1979**, *50*, 4399.
- (4) Miller, R. L.; Raison, J. Single crystals of poly(vinylidene fluoride). *J. Polym. Sci., Phys. Ed.* **1976**, *14*, 2325.
- (5) Lovinger, A. J. Crystallization of the β phase of poly(vinylidene fluoride) from the melt. *Polymer* **1981**, *22*, 412.
- (6) Priya, L.; Jog, J. P. Intercalated poly(vinylidene fluoride)/clay nanocomposites: Structure and properties. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 31.
- (7) Song, Y. M.; Zhao, Z. D.; Yu, W. X.; Li, B.; Chen, X. F. Morphological structures of poly(vinylidene fluoride)/montmorillonite nanocomposites. *Sci. China Ser. B: Chem.* **2007**, *50*, 790.
- (8) Levi, N.; Czerw, R.; Xing, S. Y.; Lyster, P.; Carroll, D. L. Properties of poly(vinylidene difluoride)-carbon nanotube blends. *Nano Lett.* **2004**, *4*, 1267.
- (9) Manna, S.; Nandi, A. K. Piezoelectric β polymorph in poly(vinylidene fluoride)-functionalized multiwalled carbon nanotube nanocomposite films. *J. Phys. Chem. C* **2007**, *111*, 14670.
- (10) Datta, J.; Nandi, A. K. Cocrystallization of poly(vinylidene fluoride) and vinylidene fluoride-tetrafluoro-ethylene copolymer blends: 3. Structural study. *Polymer* **1997**, *38*, 2719.
- (11) Guerra, G.; Karasz, F. E.; Macknight, W. J. On blends of poly(vinylidene fluoride) and poly(vinyl fluoride). *Macromolecules* **1986**, *19*, 1935.
- (12) Shah, D.; Maiti, P.; Gunn, E.; Schmidt, D. F.; Jiang, D. D.; Batt, C. A.; Giannelis, E. R. Dramatic enhancements in toughness of poly(vinylidene fluoride) nanocomposites via nanoclay-directed crystal structure and morphology. *Adv. Mater.* **2004**, *16*, 1173.
- (13) Kwon, S. M.; Kim, H. S.; Kim, D. Y.; Yun, Y. S.; Jin, H. J. Polystyrene Composites Containing Crosslinked Polystyrene-Multiwalled Carbon Nanotube Balls. *J. Appl. Polym. Sci.* **2008**, *110*, 3737.

- (14) Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys.* **1990**, *92*, 508.
- (15) Delley, B. From molecules to solids with the DMol(3) approach. *J. Chem. Phys.* **2000**, *113*, 7756.
- (16) Perdew, J. P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **1992**, *45*, 13244.
- (17) Van den Berg, A. W. C.; Bromley, S. T.; Wojdel, J. C.; Jansen, J. C. Molecular hydrogen confined within nanoporous framework materials: Comparison of density functional and classical force-field descriptions. *Phys. Rev. B* **2005**, *72*, 155428.
- (18) Khantha, M.; Cordero, N. A.; Molina, L. M.; Alonso, J. A.; Girifalco, L. A. Interaction of lithium with graphene: An ab initio study. *Phys. Rev. B* **2004**, *70*, 125422.
- (19) Dang, Z. M.; Wang, L.; Yin, Y.; Zhang, Q.; Lei, Q. Q. Giant Dielectric Permittivities in Functionalized Carbon-Nanotube/Electroactive-Polymer Nanocomposites. *Adv. Mater.* **2007**, *19*, 852.
- (20) Hasegawa, R.; Takashashi, Y.; Chatani, Y.; Tadokoro, H. Crystal structure of three crystalline forms of polyvinylidene fluoride. *Polym. J.* **1972**, *3*, 600.
- (21) Chen, Y.; Yang, D. C. Effect of quenching temperature on the crystalline structure of poly(vinylidene). *Acta. Polym. Sin.* (in Chinese) **1995**, *5*, 519.
- (22) Doktycz, S. J.; Suslick, K. S. Interparticle collisions driven by ultrasound. *Science* **1990**, *247*, 1067.
- (23) Zhao, Z. D.; Zheng, W. T.; Yu, W. X.; Long, B. H. Electrical conductivity of poly(vinylidene fluoride)/carbon nanotube composites with a spherical substructure. *Carbon* **2009**, *47*, 2118.