

Phonon states and vibration modes in one-dimensional copolymer

Da-Cheng Zhang, Jie Cheng, De-Sheng Liu, Sheng-hao Han, Liang-mo Mei, Shi-Jie Xie*

*School of Physics and Microelectronics, Shandong University, Jinan, 250100, China
Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, China*

Abstract

Lattice vibration in one-dimensional copolymer chains was studied in the framework of a tight-binding model including the interfacial coupling between homopolymer segments. The vibration density of states was obtained numerically and the characteristic of the vibration modes was recognized. It was found that there exist two types of modes, confined and hybridized. Interface modes might appear at a strong interfacial interaction. The characteristic of the organic quantum well or superlattice of a copolymer chain was discussed from the point of the lattice vibration.

© 2004 Elsevier B.V. All rights reserved.

PACS: 82.35.Jk; 43.40.-r; 68.65.-k; 73.90.+f

Keywords: Lattice vibration; Copolymer; Density of states

1. Introduction

During the past two decades, organic polymers have become an important field of investigation due to their very special properties. In addition to the desired mechanical and chemical properties, a polymer can be made into a good electric conductor after suitable doping [1,2], which originate from its highly delocalized and polarizable π -electronic clouds [3–5]. This sort of materials has generated much interest once again since the discovery that a conjugated polymer, poly(paraphenylene vinylene) (PPV), can be used as the active component in a light-emitting diode (OLED) [6,7]. Superiority of physical and chemical characteristics of polymers have already led to a new material scientific revolution [8–11].

In the chemical terminology, conjugated polymers are named as homopolymers, Most of them have a simple and quasi-one-dimensional structure, such as polyacetylene (PA), poly(*p*-phenylene) (PPP), polythiophene (PT) and

polyphenylene vinylene (PPV), etc. The band structure of a homopolymer is usually not easy to be changed, and therefore, the emitting color of a homopolymer is flat and its light-emitting efficiency will not be improved easily. However, two or more different homopolymer segments can be combined together to form a hetero-structure through physical and chemical methods. Such kind of hetero-structure is usually called a copolymer. It is expected by controlling of hetero-structures to improve the physical properties.

Extensive investigations have been evolved to understand the properties of copolymers [12–19]. Most of the researches worked on the electronic structure and photoelectric characteristic of copolymers. Some experimental work has been carried out to study the synthesis process and molecular structure of copolymers. Spectroscopic features in the Raman spectrum of both crystalline and amorphous syndiotactic polypropylenes were reported [20]. By investigating the synthesis process of organically modified silane hybrid polymers, Raman spectroscopy has proved its considerable potential in technological process diagnostics. In this paper, the vibration characteristics of three kinds of hetero-structures (diblock, triblock or sequential copolymer chain) have been studied theoretically. The next section gives the

* Corresponding author. School of Physics and Microelectronics, Shandong University, Jinan, 250100, China. Tel.: +86 5318567035x8317; fax: +86 5318567031.

E-mail addresses: xsj@sdu.edu.cn, mlm@sdu.edu.cn (S.-J. Xie).

theoretical model and the formula. In Section 3, the numerical calculations for a copolymer $-(\text{PPP})_m-(\text{PA})_n-$ are presented. The vibration modes, frequencies or the density of states are discussed. Finally in Section 4, a summary is given.

2. Model and formula

We will carry out the investigation in a copolymer chain $-(\text{PPP})_m-(\text{PA})_n-$, which consists of phenyls and acetylenes. $m=0$ and $n=0$ denote the simple polyacetylene (PA) and poly(*p*-phenylene) (PPP), respectively. Therefore, copolymer $-(\text{PPP})_m-(\text{PA})_n-$ can be also considered as a synthesis of PA and PPP (homopolymer) segments. Fig. 1 shows the molecular structure of diblock copolymer $-(\text{PPP})_m-(\text{PA})_n-$. Homopolymer segments interact each other and form σ -bonds at interface through the boundary atoms. The delocalized π -electrons are able to transfer from one segment to another through the connecting σ -bond. From this point, a copolymer molecular can still be considered as a quasi-one-dimensional chain. Most theoretical and experimental investigations have also revealed the one-dimensional characteristic of copolymers [19]. In the framework of a tight-binding approximation, the Hamiltonian describing a copolymer chain could be written as,

$$H = - \sum_{n,s} t_{n,n+1} (C_{n+1,s}^+ C_{n,s} + C_{n,s}^+ C_{n+1,s}) + \sum_n \frac{1}{2} K_n (u_{n+1} - u_n)^2 + \sum_n \frac{1}{2} M \dot{u}_n^2 \quad (1)$$

where $t_{n,n+1}$ is the electron transition integral between site n and $n+1$, which is modulated due to the possible lattice distortion. u_n is the n th atom deviation along the direction of the chain compared to the uniform structure, $C_{n,s}^+$ ($C_{n,s}$) the electron creation (annihilation) operator at site n with spin s , and K_n the elastic constant. The last term stands for the kinetic energy of the CH unit with mass M .

We set the parameters for different segment as follows, within segment PA, $t_{n,n+1}^{\text{PA}} = t_{\text{PA}} - \alpha_{\text{PA}} (u_{n+1} - u_n)$, $K_n = K_{\text{PA}}$ [21,22], within segment PPP, $t_{n,n+1}^{\text{PPP}} = t_{\text{PPP}} - \alpha_{\text{PPP}} (u_{n+1} - u_n) - t_1^{\text{PPP}} \cos n\pi/2$, $K_n = K_{\text{PPP}}$ [23], where t_{PA} (t_{PPP}) is the transfer integral in a uniform (undimerized) lattice, α_{PA} (α_{PPP}) the electron–phonon coupling parameter. t_1^{PPP} is a small value introduced to preserve the four-period structure of PPP.

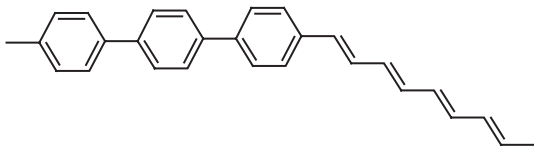


Fig. 1. Molecular structure of diblock copolymer $-(\text{PPP})_m-(\text{PA})_n-$ for $m=3$ and $n=4$.

The interaction at the at the interfacial bonds of the segments is defined as,

$$t_{\text{PA-PPP}} = \frac{1}{2} \beta (t^{\text{PA}} + t^{\text{PPP}}), \quad K_{\text{PA-PPP}} = \frac{1}{2} \beta (K_{\text{PA}} + K_{\text{PPP}})$$

where β is a parameter.

For a small deviation from the equilibrium configuration $\{u_n^0\}$, we can drive the vibration matrix of the units and the static condition through a perturbation theory, which are given by,

$$K_n (u_n^0 - u_{n+1}^0) - K_n (u_{n-1}^0 - u_n^0) = 2\alpha_n \sum_{\mu,s}' Z_{\mu,n,s} Z_{\mu,n+1,s} - 2\alpha_{n-1} \sum_{\mu,s}' Z_{\mu,n,s} Z_{\mu,n-1,s} \quad (2)$$

$$B_{m,n} = (K_n \delta_{m,n} + K_{n-1} \delta_{m,n-1} + K_n \delta_{m,n+1} + K_{n-1} \delta_{m,n}) + 2 \sum_{\mu(\mu\nu),s}' \frac{C_{\mu\nu}^m C_{\mu\nu}^n}{\epsilon_\mu - \epsilon_\nu} \quad (3)$$

where $C_{\mu\nu}^m = \alpha_{m-1} (Z_{\mu,m,s} Z_{\nu,m-1,s} + Z_{\mu,m-1,s} Z_{\nu,m,s}) - \alpha_m (Z_{\mu,m+1,s} Z_{\nu,m,s} + Z_{\mu,m,s} Z_{\nu,m+1,s})$, $\psi_{\mu,s} = \sum_n Z_{\mu,n,s} |n\rangle$ is the eigenstate of π -electron with spin s . The prime means sum over the occupied electronic states.

The calculation procedure is as following. First, the electronic Hamiltonian is solved with an initial configuration $\{u_n\}$. Substitute the eigenstates into Eq. (3) to find a new configuration. The calculation will be repeated with this new configuration. The criterion for the self-consistency is that the difference between values of u_n (in unit of nm) from two successive iterations is less than 10^{-6} . Then the vibration frequency ω_μ and the corresponding modes can be obtained by diagonalizing the matrix B_{mn} .

In order to analyze the vibration spectra in different copolymer conformations, we calculated the vibration density of state $\rho(\omega)$ from a Gaussian line shape formulae,

$$\rho(\omega) \sum_{\mu} \frac{n_{\mu}}{(2\pi\lambda)^{1/2}} \exp \left[- \frac{(\omega - \omega_{\mu})^2}{2\lambda^2} \right] \quad (4)$$

where ω_{μ} is eigen-frequency, n_{μ} is the occupation number and λ a phenomenological Gaussian line width, which we choose as $\lambda = 4.5 \text{ cm}^{-1}$.

3. Results and discussion

The parameters used for homopolymer PA are $t_{\text{PA}} = 2.5 \text{ eV}$, $K_{\text{PA}} = 1870 \text{ eV/nm}^2$, $\alpha_{\text{PA}} = 42 \text{ eV/nm}$, which correspond to a band gap of $E_g = 1.92 \text{ eV}$. For PPP, $t_{\text{PPP}} = 2.5 \text{ eV}$, $K_{\text{PPP}} = 2100 \text{ eV/nm}^2$, $\alpha_{\text{PPP}} = 48 \text{ eV/nm}$ and the degeneracy breaking parameter $t_1^{\text{PPP}} = 1.0 \text{ eV}$, which correspond to $E_g = 3.32 \text{ eV}$. The calculated band gaps of these two homopolymers are consistent with the experimental data [24–26].

It is known that for the ground state of PA, there are two branches of frequency. The lower one is the acoustic branch denoting the collective vibration of atoms in one unit cell,

Download English Version:

<https://daneshyari.com/en/article/9812863>

Download Persian Version:

<https://daneshyari.com/article/9812863>

[Daneshyari.com](https://daneshyari.com)