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Polymer 46 (2005) 7386–7393

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Vibrational dynamics and heat capacity in syndiotactic poly(propylene) form II

Vikal Saxena, Radha Mohan Misra, Poonam Tandon*, Vishwambhar Dayal Gupta

Physics Department, Lucknow University, University Road, Lucknow, Uttar Pradesh 226 007, India

Received 21 December 2004; received in revised form 11 June 2005; accepted 14 June 2005
Available online 14 July 2005

Abstract

Normal modes and their dispersion are obtained for planar-zigzag form II (*tttt*) of syndiotactic polypropylene (sPP) in the reduced zone scheme using Urey–Bradley force field and Wilson's GF matrix method as modified by Higgs. It is observed that this all *trans* backbone conformation can be characteristized by a band at 1233 cm^{-1} (calculated at 1239 cm^{-1}). A comparison is made with the spectra of its isotactic and helical form. Characteristic features of the dispersion curves such as crossing, repulsion and von Hove type singularities (regions of high density-of-states) have been explained. Heat capacity obtained from the density-of-states agrees with the experimental data up to 250 K at which the glass transition sets in and the experimental curve exhibits a marked change in slope.

Keywords: Polypropylene; Syndiotactic; Dispersion curves

1. Introduction

Polypropylene, an important fiber forming polymer, is known to exist in two tactic forms, i.e. isotactic and syndiotactic. Isotactic form has been well studied by Takeuchi et al. [1]. They have specially studied methyl torsion using inelastic neutron scattering and normal coordinate analysis. However, relatively less work have been done on the softer syndiotactic form. The syndiotactic form is known to crystallize in three different conformational states; helical form I, with *ggtt* as a repeat unit is the most common form [2–4], form II has an all *trans* sequence (*tttt*) [5], and form III conformationally ($t_2g_2t_6g_2$) assumes some of the conformational features of both forms I and II [6]. Here *g* and *t* denote *gauche* and *trans* conformational states, respectively, and the subscript stands for the number of such residues in a repeat unit.

The vibrational dynamics of syndiotactic polypropylene (sPP) of both forms I and II has been studied by several workers, e.g. Schactschneider and Snyder [7], Zerbi and Masetti [8] and others [7–10]. Most of this work is limited either by the use of approximate force field, lack of dispersion curves and their eventual use in obtaining thermodynamic parameters. Such infirmities seriously affect not only assignments but also the profile of dispersion curves, which in turn, affect density-of states and thermodynamic parameters such as heat capacity as a function of temperature. Recent studies [11] on thermal degradation of syndiotactic polypropylene show that the syndiotactic form is thermally more stable and more flexible as compared to the isotactic polypropylene. This is also supported by the relative magnitude of force constants.

In the present communication, we have accounted for all these infirmities by using Urey–Bradley force field (UBFF), which considers non-bonded interactions both in the gem- and tetra-configuration. The dispersion curves, density-of-states and heat capacity (10–460 K) thus obtained agree well with the Athas Data Update [12]. A comparative study of the isotactic and syndiotactic forms (forms I and II) is made to identify conformational sensitive modes and other spectral differences due to different orientation of the side group.

2. Theory

2.1. Calculation of normal mode frequencies

Normal mode calculation for a polymeric chain was

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* Corresponding author. Tel.: +91 522 278 2653.
E-mail address: poonam_tandon@hotmail.com (P. Tandon).

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doi:10.1016/j.polymer.2005.06.045

carried out using Wilson's GF matrix method [13] as modified by Higgs [14] for an infinite polymeric chain. The vibrational secular equation to be solved is

$$|G(\delta)F(\delta) - \lambda(\delta)I| = 0, \quad 0 \le \delta \le \pi \tag{1}$$

where δ is the phase difference between the modes of adjacent chemical units, $G(\delta)$ is the inverse kinetic energy matrix and $F(\delta)$ is the force field matrix for a certain phase value. The frequencies ν_i in cm^{-1} are related to eigen values by

$$\lambda_i(\delta) = 4\pi^2 c^2 \nu_i^2(\delta) \tag{2}$$

A plot of $\nu_i(\delta)$ versus δ gives the dispersion curve for the ith mode. The use of the type of force field is generally a matter of one's chemical experience and intuition [15]. In the present work we have used Urey–Bradley force field [16] Which has certain advantages over other fields such as valance force field etc. In the UBFF (1) relatively less parameters are required to express the potential energy, (2) no quadratic cross terms are included, the interaction between non-bonded atoms in gem- and tetra-configuration can be included and (3) the arbitrariness in choosing the force constants is reduced. Recently spectroscopically effective molecular mechanics models have been used for inter and intra molecular interactions consisting of charges, atomic dipoles and Vander Waals interactions [17].

2.2. Calculation of specific heat

Dispersion curves can be used to calculate the specific heat of a polymeric system. For a one-dimensional system the density of states function or the frequency distribution function expresses the way energy is distributed among the various braches of normal modes in the crystal, is calculated from the relation

$$g(\nu) = \sum \left[\left(\frac{\partial \nu_j}{\partial \delta} \right)^{-1} \right]_{\nu_j(\delta)=\nu_j} \tag{3}$$

The sum is over all the branches j. Considering a solid as an assembly of harmonic oscillators, the frequency distribution $g(\nu)$ is equivalent to a partition function. The constant volume heat capacity can be calculated using Debye's relation

$$C_\mathrm{v} = \sum g(\nu_j) K N_\mathrm{A} \left(\frac{h\nu_j}{KT} \right)^2 \left[\frac{\exp(h\nu_j/KT)}{\{\exp(h\nu_j/KT) - 1\}^2} \right] \tag{4}$$

with $\int g(\nu_i)\mathrm{d}\nu_i = 1$ the constant-volume heat capacity C_v, given by above equation, can be converted into constant-pressure heat capacity C_p using the Nernst–Lindemann approximation [18]:

$$C_\mathrm{p} - C_\mathrm{v} = 3RA_0 \frac{C_\mathrm{p}^2 T}{C_\mathrm{v} T_\mathrm{m}^0} \tag{5}$$

where A_0 is a constant often of a universal value [3.9×10^{-3} K mol/J] and T_m^0 is the estimated equilibrium melting temperature, which is taken to be 460.7 K [12].

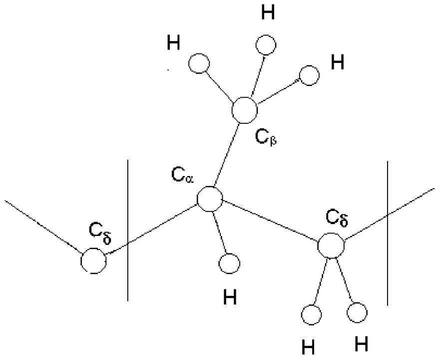

Fig. 1. One chemical repeat unit of sPP.

3. Results and discussion

A chemical repeat unit of sPP is shown in Fig. 1. The conformational repeat unit of sPP consists of two such chemical repeat units containing 18 atoms, which give rise to 54 dispersion curves. The frequencies of vibrations have been calculated for phase values ranging from 0 to π at an interval of $.05\pi$. Initially, force constants were transferred from syndiotactic poly (4-methyl, 1-pentene) [19] and then modified to obtain the 'best fit' to the observed infrared (FTIR) spectra [7]. The final force constants along with the internal coordinate are given in Table 1. Since the modes above 1350 cm^{-1} are non-dispersive in nature, dispersion curves are plotted in Figs. 2(a) and 3(a) for the modes below

Table 1
Internal coordinates and Urey–Bradley force constants (md/Å)

Internal coordinates	Force constants
$\nu[C_\beta–H]$	4.200
$\nu[C_\delta–H]$	4.150
$\nu[C_\alpha–H]$	4.360
$\nu[C_\alpha–C_\delta]$	3.300
$\nu[C_\alpha–C_\beta]$	3.700
$\varphi[H–C_\delta–H]$	0.390 (0.340)
$\varphi[H–C_\beta–H]$	0.405 (0.295)
$\varphi[C_\alpha–C_\delta–H]$	0.495 (0.255)
$\varphi[C_\delta–C_\alpha–H]$	0.540 (0.220)
$\varphi[C_\beta–C_\alpha–H]$	0.550 (0.210)
$\varphi[C_\alpha–;C_\beta–H]$	0.370 (0.200)
$\varphi[C_\alpha–C_\delta–C_\alpha]$	0.480 (0.175)
$\varphi[C_\delta–C_\alpha–C_\delta]$	0.500 (0.240)
$\varphi[C_\delta–C_\alpha–C_{\beta]}$	0.600 (0.220)
$\tau[C_\alpha–C_\delta]$	0.008
$\tau[C_\alpha–C_\beta]$	0.008
$\tau[C_\delta–C_\alpha]$	0.008
Off-diagonal interactions	
$\nu[C_\alpha–C_\delta] - \varphi[C_\alpha–C_\delta–H]$	0.300
$\nu[C_\alpha–C_\beta] - \varphi[C_\beta–C_\alpha–H]$	0.400

Note: ν, φ, ω, τ denote stretch, angle bend, wag and torsion, respectively. Stretching force constants between the non-bonded atoms in each angular triplet (gem configuration) are given in parentheses.