Analysis Method

In situ Raman spectroscopic investigation of olefin multiblock copolymers during melting and crystallization

Zhijun Nie, Peng He, Wei Yu*, Chixing Zhou

Advanced Rheology Institute, Shanghai Key Laboratory of Electrical Insulation and Thermal Ageing, State Key Laboratory for Metal Matrix Composite Materials, Department of Polymer Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, PR China

A B S T R A C T

The crystallization behaviors of olefin multiblock copolymers were investigated by Raman spectroscopy. A new approach was proposed to fulfill the Raman three phase analysis. The crystallinity obtained from such approach is well consistent with the method using melt Raman spectrum as a reference. It is found that both the Raman total crystalline fraction and the Raman orthorhombic crystalline fraction are affected by the hard block content of OBCs. Non-isothermal experiments on melting and crystallization illustrate that Raman spectrum and DSC can give identical transition temperatures. However, Raman spectrum analysis shows two distinct features during crystallization and melting of OBCs, namely the disappearance of all-trans noncrystalline phase at temperature much higher than the melting point and the dynamic balance of the interfacial phase fraction.

1. Introduction

Polyethylenes are one of the most frequently used synthetic polymers in the world [1]. High-density polyethylene, low-density polyethylene, and linear low-density polyethylene are found in a myriad of applications. Development of new state-of-the-art materials by modifying polyethylene structure and, as consequence, its properties is an important area of fundamental research. A well-known way to tune the structure and properties is the incorporation of α-olefin to form random copolymers or block copolymers [2]. As an example, olefin block copolymers (OBCs) using the chain-shuttling technology [3] has been commercialized recently, which are statistically linear multiblock copolymers of alternating soft segments (high octene content) and hard segments (low octene content). The soft segment is amorphous blocks having a low glass transition temperature, while the hard segment is crystallizable having a high melting point close to that of high-density polyethylene [4].

Crystallization is one of the most important behaviors of polymers. The commonly used testing methods for monitoring crystallization are differential scanning calorimetry (DSC), wide angle (WAXS) and small angle (SAXS) X-ray diffraction, nuclear magnetic resonance (NMR), infrared (IR) spectroscopy and Raman spectroscopy [5]. Among these techniques, Raman spectroscopy and NMR are the two methods which can provide direct evidence for the existence of the interfacial phase in semicrystalline polymers [6,7]. It is well known that Raman spectroscopy is a spectroscopic technique to observe vibrational, rotational,

and other low-frequency modes in a system [8]. Because vibrational information is specific to the chemical bonds and symmetry of molecules, it is commonly used in chemistry and polymers.

For polyethylene, the analysis of the Raman internal modes has offered a quantitative procedure to establish the phase structure [5,6]. In the past thirty years, Raman spectroscopy has been used extensively for the analysis of polyethylene [5,6,9–14] and ethylene random copolymers [12,15,16]. In order to determine the integrated intensities, several methods have been proposed for separating the overlapping bands. The original method is a manual decomposition [6,10]. Later, computer decomposition and curve fitting was adopted to improve the accuracy [5,11,17]. Keresztury used least-squares curve analysis with a fixed 60% Gaussian and 40% Lorentzian fitting for the Raman spectra of polyethylene. They commented that the manual decomposition method led to overestimated amorphous contents at the expense of the interfacial contents [17]. Although the floating Gaussian/Lorentz fitting method gives a better fitting than the fixed 100% Gaussian fitting, the crystalline fraction of the polymer could not be detected by the floating Gaussian/Lorentz fitting method [5]. The reliability and precision of the decomposition methods is always challenge in this analysis. Alternative approach is to use the Raman spectrum of melt as a reference [9]. However, Raman spectroscopic study of ethylene block copolymers is still rare. What's more, in situ Raman spectroscopic study of polyethylene and ethylene/olefin copolymers during its melting and crystallization is still far from been revealed.

In the preceding work, we have explored the melt-phase behaviors

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Table 1
Molecular parameters of olefin multiblock copolymers.

Sample code	M_W (kg/mol)	PDI	X_c (wt%)	f_{hard} (wt%)	total C_8 (mol%)	T_{MST} (°C)	Mesophase separation
L01	79.8	1.97	7.4	11.0	13.7	163.5	Extremely weak
L02	126.5	2.06	7	11.0	14.0	> 200	Strong
M01	61.7	1.83	14.0	25.0	11.7	153.8	Extremely weak
M02	82.6	2.15	14.8	25.0	12.0	160.4	Medium
M03	156.6	1.97	14.3	25.0	11.5	> 200	Very strong
H01	77.6	1.92	22.7	35.0	9.6	154.0	Medium

of a series of OBCs with varying block structures [4]. Based on the understanding of the melt structures, we further investigated the liquid–solid transitions of OBCs during crystallization and clarify the influence of melt structure on the large-scale network formation during crystallization [18]. In this paper, we will focus our attention on the crystallization behavior of OBCs via Raman spectroscopy.

2. Experimental section

2.1. Materials

The OBCs synthesized via the chain-shuttling technology were provided as pellets by The Dow Chemical Company [3]. Six low octene content OBCs with different block structure were selected in this work. The detailed information on molecular structure is given in Table 1. The octene content (C_8) and block structure of OBCs were determined by ^{13}C NMR, the molecular weight (M_w) and polydispersity index (PDI = M_w/M_n) were measured by high temperature gel permeation chromatography (GPC). Details about the characterization have been reported in our previous publication [4,18,19]. These six OBCs are identified by the codes $H_x/M_x/L_x$, where H/M/L reflects the relatively high/medium/low content of hard block, and the subscripts x are numbers that increase with the total molecular weight. The main differences between the six OBCs are the total hard block content and the molecular weight. The difference between the octene content in hard segment and soft segment (ΔC_8) is similar in all six samples, which implies similar interaction between hard segment and soft segment in these samples. Then, the phase separation behavior is mainly determined by the molecular weight and the hard block content [4].

2.2. Measurements

2.2.1. Thermal analysis

Thermal analysis was performed by a differential scanning calorimeter (DSC, Q2000 TA instruments). The instrument was calibrated with indium and tin. All experiments were performed in nitrogen atmosphere with a flow rate of 50 mL/min. For OBCs, the heating and cooling thermograms were conducted between −50 and 200 °C with a rate of 10 °C/min. The first cooling scans and the second reheating scans were taken for determining the crystallization and melting transition temperatures. The crystallinity was calculated according to the following equation:

$$X_C = \frac{\Delta H_m}{\Delta H_m^0} \qquad (1)$$

where ΔH_m is the fusion enthalpy of the sample and ΔH_m^0 is the theoretical fusion enthalpy of the perfect crystalline polyethylene (ΔH_m^0 = 292 J/g).

2.2.2. Raman spectroscopy

The Raman spectroscopy (Ocean Optics, QE65 Pro) with a 785 nm

laser was used to collect the Raman spectra. Diameter of the laser spot on the sample surface was adjusted to be about 10 μm in order to prevent local overheating of the sample and changing its structure. To avoid the influence of edge effects, Raman spectra were recorded in the central part in width of the samples. Raman spectra were collected with the same measurement parameters (6 s integration time, 5 accumulations, 100 mW laser power at the sample). The thermal treatments were the same as that in thermal analysis measurements. In order to monitor the crystallization and melting process, the Linkam Optical System (CSS450) was used to precisely control the temperature. It is noted that the size of the OBCs sample should be chosen as small as possible in order to quickly achieve thermal equilibrium during crystallization and melting.

3. Results and discussions

3.1. Thermal behaviors of OBCs

Before investigating the process of the crystallization and melting by the Raman spectroscopy, it was necessary to understand the thermal behavior of OBCs. The DSC curves of crystallization and the subsequent melting of OBCs are shown in Fig. 1. The values of crystallization temperatures (T_c), as well as melting temperatures (T_m) are labeled. There are obvious differences between transition temperatures due to the different molecular weight and hard block content. The melting and
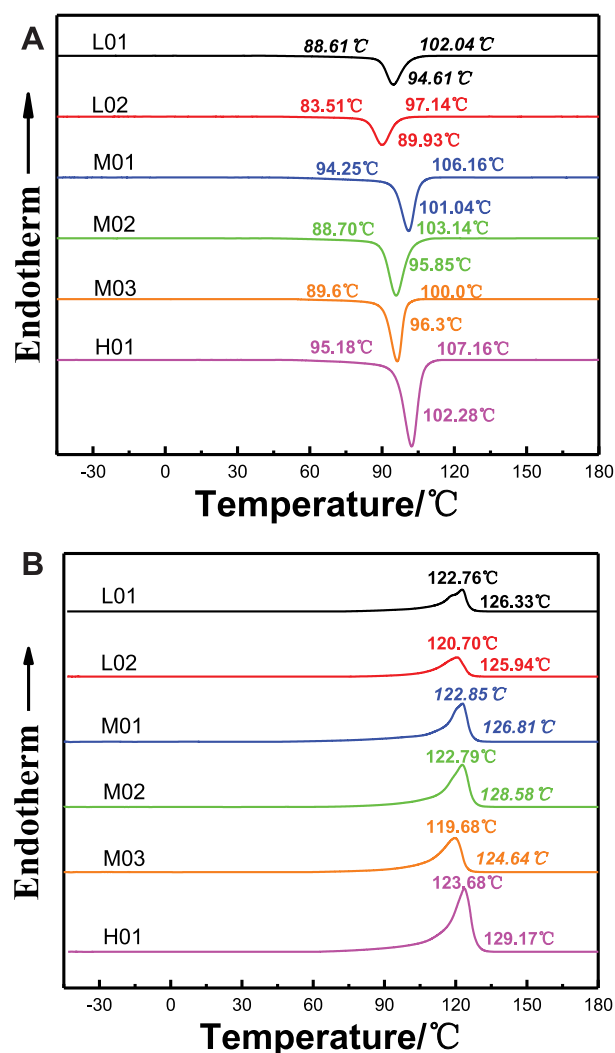

Fig. 1. Thermal behavior of OBCs: (a) the crystallization process; (b) the melting process. The heating/cooling rate was 10 °C/min.