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Thermal degradation of syndiotactic polypropylene and the influence of stereoregularity on the thermal degradation behaviour by in situ FTIR spectroscopy

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Abstract

The thermal degradation of syndiotactic polypropylene (sPP) and the influence of stereoregularity on the thermal degradation behaviour have been studied by in situ Fourier transform infrared (FTIR) spectroscopy. With the aid of the time-resolved FTIR, the conventional kinetic parameters, such as the degradation activation energy ΔE and the degradation factor n, can be calculated. The experimental results show that sPP decomposes by random chain scissions. More importantly, the difference of degradation activation energy from some characteristic absorption bands shows that the thermal degradation of sPP is a multi-step process, which is further confirmed by the principal components analysis (PCA). Comparing with isotactic polypropylene (iPP), the main chain of sPP is more flexible, therefore the thermal stability of sPP is much higher than iPP.

Keywords: Thermal degradation; Syndiotactic polypropylene; Isotactic polypropylene; In situ FTIR spectroscopy; Multivariate analysis

1. Introduction

In the past few years, a number of studies have been conducted on the thermal degradation and kinetic analysis of polypropylene (PP) using various methods [1–5]. The effect of stereoregularity on the thermal degradation of PP has become an interest in both scientific research and engineering applications. In terms of the stereoregularity, polypropylene can be divided into isotactic, syndiotactic and atactic polypropylene (iPP, sPP and aPP). The difference in the thermal degradation between iPP and aPP has been studied intensively, and it was concluded that iPP was more susceptible to oxidation than aPP [6–10]. However, due to the low stereoregularity of sPP synthesized by a conventional vanadium-based catalyst, only a little attention had been paid to sPP before the 1990s. In 1988, Ewen and coworkers succeeded in using a metallocene catalyst to prepare highly stereoregular syndiotactic polypropylene with high molecular weight [11]. Since then, the structure, morphology and physical properties of sPP have been widely studied, and it is found that the thermal stability of PP is dominantly determined by stereoregularity [12–15]. Heat treatments

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and chemiluminescence were used to compare the thermo-oxidative stability of iPP and sPP. Under the same degradation condition, iPP is decomposed more drastically in comparison with sPP, indicating that sPP has much higher thermal stability than iPP [12–15]. Although such consideration provides grounds for thermal stability of sPP, the exact decomposition kinetic parameters such as the degradation activation energy ΔE and the degradation factor n are not fully provided and few studies are focused on the comparison of conformational change between iPP and sPP during the thermal degradation.

There are several experimental methods to characterize the thermal degradation of polymers, and thermogravimetric (TG) analysis is one of the most commonly used because of the simple experimental principle and process, accurate experimental data, and straightforward analysis. Unfortunately, in spite of the popular application of TG in thermal degradation, a major drawback of this analysis method is that it cannot directly provide molecular structure change during the degradation process. Recently, we developed a novel approach, in situ Fourier transform infrared (FTIR) spectroscopy, to investigate on-line the thermal degradation of isotactic polypropylene (iPP) from macroscopic molecular thermodynamics and microscopic molecular conformation [16,17]. This new method of studying thermal degradation of polymers not only shows the conventional kinetic parameter information of thermal degradation such as the degradation activation energy ΔE and the degradation factor n, which are in accord with the results of traditional thermogravimetry experiments, but also indicates some significant molecular structure changes during the thermal degradation process. Moreover, the spectral uncertainty and experimental errors can be reduced greatly by analysing the entire spectrum with a multivariate approach. In this paper, we firstly adopt this new technique to study the thermal degradation behaviour of sPP, and then further discuss the influence of stereoregularity on the thermal degradation behaviour of polypropylene.

2. Experimental

2.1. Materials

The iPP and sPP samples used in this study were kindly supplied by Shanghai Jinshan Petrochemical Corp., Shanghai, China, and Dow Chemical Company, U.S.A., respectively. The isotacticity of the iPP sample is approximately 94.5%, and the melt flow index is 3.0 g/10 min. The syndiotacticity of the sPP sample is approximately 90.0%, and the melt flow index is 2.9 g/10 min.

2.2. Measurements

2.2.1. In situ Fourier transform infrared spectroscopy (FTIR)

The IR spectra were collected at a resolution of 4.0 cm^{-1} using a Bruker Equinox-55 FTIR spectrometer equipped with a variable temperature cell under a flowing nitrogen atmosphere. The film samples of iPP and sPP, about 20 μm thick, were heated from room temperature (20 °C) to 450 °C at a heating rate of 10 °C/min. At the same time, the FTIR spectra were recorded at the rate of one spectrum per 4 s. Thus the relationship of IR intensity with temperature can be obtained. Since each band has its own intensity coefficient, the IR intensities of observed bands have been normalized to the maximum values. The temperature was carefully calibrated and the scanned wavenumber range was 4000–400 cm^{-1}. The details of in situ FTIR experiments have been reported previously [16–25]. The iPP sample began to degrade at about 240 °C and the degradation ended at about 400 °C. The sPP sample began to degrade at about 260 °C and the degradation ended at about 420 °C.

2.2.2. Thermogravimetric analysis (TG)

Thermogravimetric analysis was performed with a TA Instruments Model 2050 thermogravimetric analyser in nitrogen at a gas flow rate of 40 ml/min with iPP and sPP sample weights of 0.6690 mg and 0.6540 mg, respectively. The heating rate was 10 °C/min, and the iPP and sPP samples were degraded from 240 °C to 400 °C and from 260 °C to 420 °C, respectively.

2.2.3. Differential scanning calorimetry analysis (DSC)

Differential scanning calorimetry (DSC) traces were recorded with a Perkin–Elmer Pyris-1 Series differential scanning calorimeter under a flowing nitrogen atmosphere. The DSC was carefully calibrated with In and Zn standards before measurement. The heating rate was 10 °C/min and the weight of iPP and sPP samples used in DSC were approximately 2.0 mg and 2.1 mg, respectively. The obtained result shows that the melting temperatures of iPP and sPP samples used in IR measurement are 161 °C and 152 °C, respectively.

2.2.4. Multivariate analysis

The IR data were dealt with by using principal components analysis (PCA), one of the most commonly used multivariate analysis techniques. PCA model was built by using the Matlab 6.5 software.