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Evaluation on the degrading behavior of melt polyolefin elastomer with dicumyl peroxide in oscillatory shear flow by Fourier transform rheology

Jianye Liu, Wei Yu*, Chixing Zhou

Advanced Rheology Institute, Department of Polymer Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

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Abstract

The degradation of melt polyolefin elastomer (POE) at the presence of dicumyl peroxides (DCP) was estimated at elevated temperature in oscillatory shear flow. Large amplitude oscillatory shear (LAOS) experiments followed by Fourier transform rheology (FTR) were carried out to detect and evaluate the branching architecture of the products. The third complex harmonic (I_3*) and other two parameters, small strain elastic shear modulus (M) and large strain elastic shear modulus (L), which describe the nonlinearity and elasticity of a material obtained from FTR, are mainly used to characterize the topological structure of polymer chains. The results indicate the degradation appeared just after a large amount of the long chain branches (LCB) created rather than as soon as the reaction started when the strain was applied within the linear viscoelastic regime of the original POE at high frequencies. This is different from our previous result that the dominant reaction was coupling in linear shear flow. The threshold strain for degradation decreased with the oscillatory frequency, and the frequency owned a different acting mechanism from the strain amplitude to cause the degradation reaction. Moreover, there is a kind of selectivity of shear rate on the polymer chains for degradation. Low frequency results in short linear scission segments and a long branched chain suffers from degradation more than once. At high frequency, the possibility of degradation at the sites near the branching points of LCB increases.

Keywords: POE; Oscillatory shear flow; Degradation

1. Introduction

In our previous paper [1], the effect of shear flow on the reaction of polyolefin elastomer (POE) at the presence of peroxides at elevated temperature has been investigated. Both coupling and degrading reactions were observed. Although it is general known that the degradation occurs in the manner of β-scission, it also includes another counter course, referred to as a recombination reaction of the secondary macromolecular radical (C_R) and the polymer chain with a double bond ($C_=$) produced by β-scission. The main reaction mechanism is shown in Scheme 1 and we labeled the structure of isolated tertiary carbon with "br1" and the structure of two tertiary carbons in a chain separated by only one CH_2 group with "br2". Actually, the chain scission is possible just when the tertiary carbon radical is in the form of br2, which has been confirmed by ^{13}C NMR spectroscopy [1]. β-scission is a kind of monomolecular reaction and should be attributed to the chemical and structural properties of the reactant and independent of the shear flow field. It is even believed that β-scission could also occur in quiescent state. But the counter reaction (recombination) which is diffusion controlled can be affected by the shear flow field greatly in such entanglement system [2,3]. The key factor for the recombination is the relative distance between the active sites of C_R and $C_=$. In fact, the degradation indeed occurs just when the recombination is not dominant, so the probability of degradation of POE depends on the shear flow field imposed upon the reaction system. In

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* Corresponding author. Tel.: +86 21 54743275; fax: +86 21 54741297.
E-mail address: wyu@sjtu.edu.cn (W. Yu).

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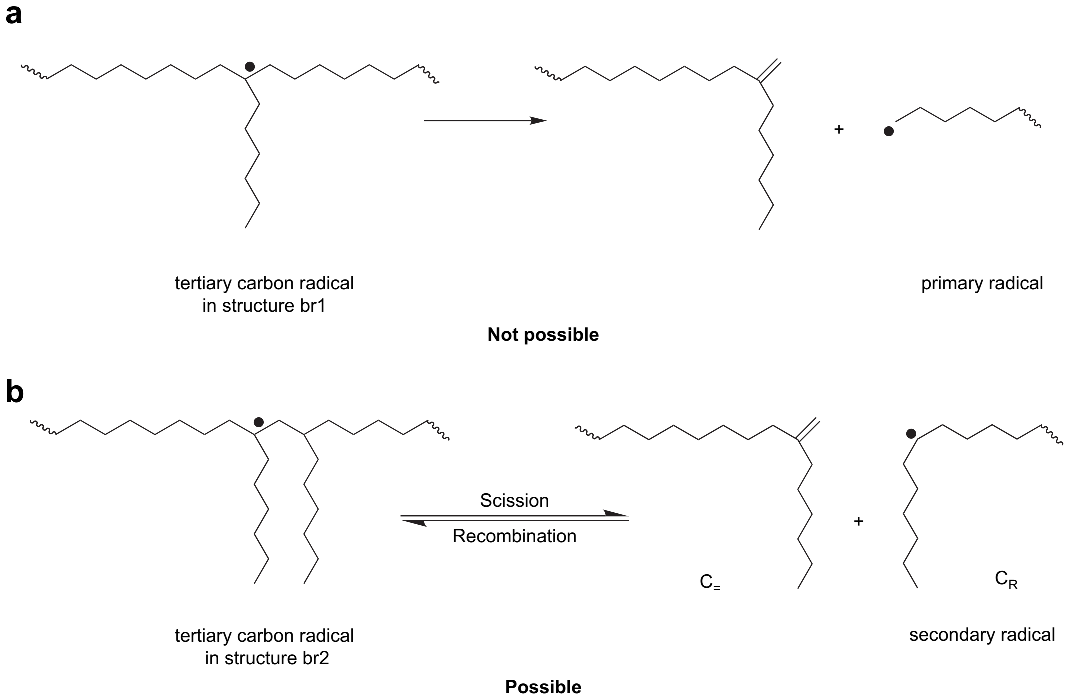

Scheme 1. Scission reactions of tertiary carbon radicals in structure br1 (a) and br2 (b).

POE/peroxide system, the coupling reaction is dominant in linear shear flow which is same as the case of polyethylene with peroxides, whereas the POE chain is also able to degrade when the strain rate exceeds the linear regime. Moreover, we found that the critical strain amplitude for the degradation of POE in oscillatory shear flow altered with the applied oscillatory frequency [1]. The applied strain amplitude and frequency seem to influence the distance between C_R and $C_=$ in different ways. So it is necessary to make clear the action mechanism of frequency and strain amplitude, including whether they have different effects on the degrading behavior of POE chains and how they act, respectively.

Usually in the system of commercial polyolefin modified by peroxides, the long chain branches (LCB) are always created by coupling reaction whereas the degradation can tailor the length of polymer chains. There are few changes in functional groups, but the molecular weight and its distribution as well as topological structures of polymer chains change a great deal. Since the polymer architecture is so crucial as to influence the reaction process and the property of final product, it is very important to understand it clearly and control it. In the usual testing methods, gel permeation chromatography (GPC) can directly give the molecular weight distribution of product but without the information of topological structure of polymer chains. The use of ^{13}C NMR is also limited because it is unable to differentiate between branches with six or more carbon atoms. However, the rheology is one suitable tool owning the advantage for determination of macromolecular structure. Due to the more complicated topological structure of LCB, the characterization is more difficult than that of the linear chain. Compared with many rheological methods such as small amplitude oscillatory shear (SAOS), vGP plot, Cole–Cole plot and stress relaxation, Fourier transform rheology (FTR) generally following the large amplitude oscillatory shear (LAOS) experiments is one more powerful rheological methodology to estimate LCB. The continuous application of LAOS is a simple way to actualize the nonlinear condition and has been proved very sensitive to the microstructure of the fluids, e.g., by Giacomine and Dealy [4], Hyun et al. [5,6]. Even though the validity of linear viscoelasticity fails with large strain amplitude, more information can be obtained through the analysis of the response in the Fourier space. The approach of FTR has already been presented by Wilhelm et al. [7–10] and Neidhöfer et al. [11,12] on the linear polymer melts and solutions and branched polymers. Fleury et al. [13], Schlatter et al. [14] and Vittorias et al. [15] have also applied this technique on the linear and branched industrial polyethylenes, the relative intensities (I_n/I_1) and phase shifts (Φ_3) of the higher harmonics between them in the frequency spectrum were distinguishing extremely. In a similar way, we can study the molecular architectures of the reaction products containing linear and branched polymers and speculate on how they are formed under shear flow field.

The purpose of this paper is to investigate how the critical strain amplitude for the degradation varies with the frequency and give the action mechanism of both the applied strain amplitude and frequency on such degrading behavior of POE chains in oscillatory shear flow. For this purpose, we have utilized LAOS followed by FTR to characterize the products created in different conditions of oscillatory shear flow. According to the analysis of rheological measurements and FTR, we could try to confirm where is the site for the effective β-scission on the polymer chain.