Polymer 122 (2017) 208–221

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Deformation X-ray study of propylene-based elastomers with controlled sequence distributions

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ARTICLE INFO

Article history:
Received 11 April 2017
Received in revised form
31 May 2017
Accepted 23 June 2017
Available online 27 June 2017

Keywords:
Deformation
X-ray
Diffraction
Scattering
Propylene
Elastomers
Sequence distributions

ABSTRACT

Three iso-specific organometallic catalysts for ethylene and propylene copolymerization with varying products of ethylene and propylene reactivity ratios were utilized to synthesize equal-molecular-weight propylene-based elastomers (PBEs) of alternating (aPBE), random (rPBE), and blocky (bPBE) backbone sequences. To compensate for the variations in catalyst iso-specificity, the ethylene content of PBEs was varied between 11 wt % and 16 wt % in order to maintain constant amount of 50% isotactic propylene trimer concentration. Their microstructural evolutions during the initial extension-retraction cycle at a low strain ranging from 0% to 100% were investigated using 2D Wide-Angle X-ray Diffraction (WAXD) and Small-Angle X-ray Scattering (SAXS) techniques. WAXD results revealed that the crystallinity values of these PBEs changed little during the extension-retraction cycle. However, SAXS results indicated that bPBE formed distinctly ordered stacked lamellae morphologies, whereas the crystalline-amorphous repeat units in aPBE and rPBE were more disordered. In addition, the long period of the bPBE lamellar structure exhibited elastic affine deformation. The analysis suggested that initially randomly arranged crystalline lamellae in PBE become partially oriented, but not destroyed, with increasing strain, where over half of the lamellar structures were orientated parallel to the stretching direction when the strain reached 100%. Upon cessation of stress, these orientated crystalline structures could recover back to their isotropic state.

1. Introduction

Desirable propylene-based elastomers (PBE) are random copolymers of propylene and ethylene (with polypropylene crystallinity and crystalline structure) that can be synthesized by coordinative insertion polymerization using an organometallic single-site catalyst. In addition to the stereo- and regio-defects introduced by the catalyst, the ethylene moiety inserted into the backbone also behaves as a chemical defect to disrupt the propylene sequences during crystallization [1]. Ziegler-Natta catalysts (such as $TiCl_3$ on $MgCl_2$ support) can synthesize isotactic propylene-ethylene copolymers at high molecular weight with good commercial catalyst activity and reaction temperature. However the $TiCl_3$ catalysts can only incorporate up to 5 wt% ethylene. Vanadium Chloride based Ziegler-Natta catalysts on the other hand will only polymerize ethylene and atactic propylene, with ethylene contents greater than 45 wt%. PBEs of propylene-ethylene copolymers of ethylene content 10–20 wt% only became a commercial reality by the discovery of C2-symmetic metallocene catalysts. We refer the interested reader to our previous publication [4] and references therein for details on metallocene catalysts that achieve stereo-control in PBEs. For a propylene-ethylene copolymer with increasing ethylene defects, its crystalline morphology could transition from spherulites to sheaf's, to crosshatched webs, to embryonic axialites, and to radial and random lamellae, while the

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http://dx.doi.org/10.1016/j.polymer.2017.06.053
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α−phase content would decrease and the γ−phase content would increase [2,3]. For example, when the ethylene content is higher than 10 wt% in PBE, its morphology revealed the mixed cross-hatched and isolated lamellae structures with both α and γ polypropylene (PP) crystallites [1,3]. Because the PP crystallite has a higher cohesive strength than the surrounding amorphous matrix, it can be considered as an effective crosslink. In other words, the classic rubber elasticity theory can be applied to PBEs if the crosslinks, including PP crystallites and chain entanglements, can stay stable during the deformation process.

It is possible that we can enhance the elasticity of PBE by raising the crystallinity (more crystallite crosslinks) and molecular weight (more entanglement crosslinks), but without changing the lamellar assembly (that would result in the crosslink loss due to crosslink aggregation). For copolymerized propylene-ethylene PBEs, this may be achieved by adjusting the crystallizable propylene sequence length at a given ethylene content through controlling the distribution of ethylene moiety in the polymer chain that can be regulated by the product of the ethylene/propylene reactivity ratios (r_1r_2) from the catalyst used. To test this hypothesis, three organometallic catalysts for propylene-ethylene copolymerization with r_1r_2 of <0.5, 1, and >2 were used to synthesize PBEs of roughly equal molecular weight and theoretical crystallinity. Since their isospecificities were different, the ethylene contents of the three PBEs were carefully adjusted to achieve constant isotactic propylene trimer content. Their elastic behaviors of these three samples, during the cyclic tensile deformation from 0 to 100% extension, were examined. The deformation strain was intentionally kept low to retain the initial crystalline morphology, where the strain-induced crystalline destruction or formation can be ignored. The results indicated that the structure and property relationships of these three samples are indeed closely correlated to their sequence distributions and the catalyst reactivity ratio [4]. Their microstructural evolutions (i.e., crystalline/amorphous structural developments) during the low-strain extension and retraction cycles were investigated by 2D WAXD and SAXS techniques, which coupled with a Linkam deformation stage that simultaneously measured their mechanical properties. This work expands on our previously reported work [4]: we study the effect of microstructure on the tensile deformation process for the three PBE materials made from iso-specific organometallic catalysts.

2. Experimental

2.1. Materials preparation

Three organometallic catalysts were selected for the preparation of alternating PBE (aPBE), random PBE (rPBE) and blocky PBE (bPBE) samples. The catalyst used for synthesizing aPBE, Catalyst 1, was a C1 symmetric non Metallocene catalyst that is known to give alternating sequence distributions. The rPBE catalyst, Catalyst 2, was a C2-symmetric dimethyl-silyl-bis(indenyl) hafnium -dimethyl precursor activated by dimethylanilinium-tetrakis(pentafluorophenyl) borate and the bPBE catalyst, Catalyst 3, was a C2-symmetric dimethyl (μ-dimethyl -silyl)-bis(2-methyl-4-naphthylindenyl) zirconium precursor activated by dimethyl−anilinium-tetrakis(heptafluoronaphthyl) borate. Details of polymer synthesis and reaction conditions are described in Ref. [4] and patents therein.

2.2. Structure characterization and elasticity

Molecular weights, molecular weight distributions, and compositions of all PBEs were measured using GPC-IR, whereas sequence distributions and compositions were determined by ^{13}C NMR. Since NMR sequence distributions of all three copolymers were found to conform to the first order Markovian statistics, their comonomer reactivity ratios were determined by the Markov model. All PBEs were compression molded into films (melt temperature of 190 °C employed) and aged for more than 7 days (to ensure completing crystallization) prior to punching out ASTM type 3 dog bone samples. It was critical for the samples to reach full crystallinity for consistent and reproducible mechanical testing. An Instron tensile tester was used for the mechanical tests at room temperature. The samples were placed in the grips with a 35-mm grip separation. Slack was manually removed so that the reading on the instrument registered a tiny but positive tensile force before starting the test. The samples were stretched to a 100% extension at 100 mm/min. The crosshead was returned to 0% extension and the cycle was repeated once more. The elasticity values, top load, set, hysteresis, and retractive force, were determined by averaging over measurements done from at least three specimens. Molecular structures, compositions, crystallinity, and elastic properties of these three PBE's are provided in Table 1. Although all three PBEs have an equal amount of crystallizable sequences, interestingly the *high-C2* (high-ethylene) bPBE had the *highest crystallinity* while the *low-C2* aPBE possessed the *lowest crystallinity*. Correspondingly, bPBE had the best elasticity, as measured by set, hysteresis, and retractive force, among the three, followed by rPBE, and then aPBE.

2.3. In-situ deformation by X-ray scattering techniques

All deformation X-ray scattering studies of PBEs were conducted using an *in-house* SAXSLAB Ganesha 300XL+ with an X-ray wavelength of 0.1541 nm from a microfocus CuKα Xenocs source. A Dectris Pilatus 300 K X-ray area detector was employed for 2D data collection and the detector can slide inside the flight tube to move from WAXS to SAXS data acquisitions as shown in Fig. 1(a). The sample-to-detector distances for WAXS and SAXS were 89.66 and 1039.89 mm, respectively, with corresponding WAXS and SAXS exposure times of 600 s and 1200 s. All experiments were carried out at fixed deformation strains of 0% → 30% → 60% → 100% → 60% → 30% →15% for the 1st extension-retraction cycle and of 15% → 30% → 60% → 100% → 60% → 30% → 15% for the 2nd extension-retraction cycle. As shown in Fig. 1 (c), the machine direction (i.e., stretching direction) is aligned vertically to the beam path.

All scattering data from SAXS and WAXS will be plotted as Intensity versus s where $s = \frac{2sin\theta}{\lambda}$ and $s = \frac{1}{d_{hkl}}$ where d_{hkl} is the unit cell lattice spacing for each (hkl) reflection.

3. Results and discussion

3.1. Deformation WAXS study

2D WAXS patterns of the three PBE samples before the deformation are shown in Fig. 2 (a) to 2(c), which exhibit similar scattering features. These images indicated an isotropic structure with a broad amorphous halo superimposed with several sharp crystal diffraction rings. The azimuthally averaged intensity profiles of the three samples are illustrated in Fig. 2(d), where all diffraction peaks (s = 1.59, 1.91, 2.27, 2.43, 2.84 and 3.24 nm^{-1}) indicate the existence of mixed α and γ phases [5]. In specific, the diffraction peaks at s = 1.59, 1.91, 2.43, 2.84 and 3.24 nm^{-1} can be indexed by both α phase and γ phase, whereas the diffraction peak at s = 2.27 nm^{-1} is the characteristic (117) reflection of the γ phase, and the peak at s = 2.09 nm^{-1} is the characteristic (130) reflection of the α phase (that is quite weak in these samples). This observation suggests that majority of the crystallites in all three PBEs are γ phase of isotactic polypropylene (i-PP). In addition, the crystal diffraction peaks of