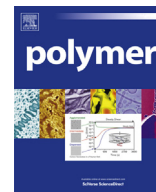




Contents lists available at ScienceDirect

Polymer

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

The chemical structure of the amorphous phase of propylene–ethylene random copolymers in relation to their stress–strain properties

Vipin Agarwal^{a,b,1}, Tim B. van Erp^c, Luigi Balzano^{b,c,f}, Markus Gahleitner^d,
Matthew Parkinson^d, Leon E. Govaert^c, Victor Litvinov^{b,e,**}, Arno P.M. Kentgens^{a,*}

^a Radboud University, Institute for Molecules and Materials (IMM), Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

^b Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands

^c Department of Mechanical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^d Borealis Polyolefine GmbH, Sankt-Peter-Strasse 25, 4021 Linz, Austria

^e DSM Resolve, P.O. Box 18, 6160 MD Geleen, The Netherlands

^f DSM Ahead, P.O. Box 18, 6160 MD Geleen, The Netherlands

ARTICLE INFO

Article history:

Received 30 October 2013

Received in revised form

21 December 2013

Accepted 25 December 2013

Available online xxx

Keywords:

Propylene–ethylene random copolymers

Solid-state NMR

Mechanical properties

ABSTRACT

A better understanding of structure–property relations is necessary to design novel materials. In this study, we investigate the morphology and chemical structure of five commercial grades of propylene-based polymers in relation to the change in yield–stress as a function of strain-rate. Substantial emphasis has been laid on understanding the chain microstructure in the relation to chain dynamics in the amorphous phase. Heterogeneous Ziegler–Natta catalysis was used to prepare the samples with differing ratios of propylene and ethylene units. Various analytical techniques such as WAXS, SAXS, solution- and solid-state NMR were employed to characterize their structure. The results indicate a reduction in crystallinity, melting temperature, long-period and crystal thickness with increasing ethylene content. Solid-state NMR data reveal the presence of four components in these samples, which is an extension of the traditional three phase model found in most semi-crystalline polymers. The additional fourth phase is attributed to a rubber-like component that is primarily composed of chain segments rich in ethylene units and shows an increase in chain dynamics with increasing ethylene content in the samples. Mechanical experiments show that yield stress decreases with increase in the amount ethylene which can be correlated to the observed increase in chain dynamics in the amorphous phase.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The physical and mechanical properties of a polymer are a complex interplay of morphology and the chemical structure of the polymer. While the chemical structures are defined during synthesis, molecular conformation and crystal morphology distributions are shaped during post-synthesis processing. The dependence of the conformation and morphology on processing conditions arises because the physical structure formation in polymers such as

polyethylene and polypropylene, is often determined by crystallization kinetics [1]. Depending on the processing conditions one can influence the relative amount of various phases, the type of crystals formed, orientation, etc. [2–12]. These variations in the structure define the resulting properties of the material.

Polypropylene (PP) is an important polymer which is often encountered in our daily life because it is an economical material with a unique combination of desirable physical, mechanical, thermal, chemical and electrical properties [13–19]. Commercially, PP is available in the form of a homopolymer, random copolymers, block copolymers and rubber modified impact copolymer. Random copolymers with small fraction of α -olefin (e.g., ethylene, butene, hexane, etc) units (0.2–7 mol%) were developed to improve properties of PP-homopolymers such as impact strength at low-temperature, clarity, stress-crack resistance and sealing temperatures as well as other properties [20–25].

* Corresponding author.

** Corresponding author. DSM Resolve, P.O. Box 18, 6160 MD Geleen, The Netherlands.

E-mail addresses: Victor.Litvinov@dsm.com (V. Litvinov), A.Kentgens@nmr.ru.nl (A.P.M. Kentgens).

¹ Current address: Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland.

A number of methods have been employed to understand the structure of semi-crystalline polymers. On a molecular level, most experimental techniques differ with respect to their sensitivity in detecting various phases in the polymer. In order to understand structure–property relationships it is necessary to elucidate the chemical and physical structures of each phase in terms of phase composition, domain sizes, microstructure, conformation and chain dynamics. NMR spectroscopy has become an indispensable tool for the characterization of polymers. Typically high-resolution solution-state NMR spectroscopy allows identification and quantification of the various microstructures formed during polymerization. For example, the comonomer content, degree of branching, comonomer sequence distribution, tacticity, content of regio-defects and amount of end groups in PP copolymers can all be determined from a single quantitative ^{13}C solution-state NMR spectrum [26–29]. In contrast, solid-state NMR probes polymers in their native state and under conditions that are identical to their application environment. It provides a snapshot of the ensemble of all chains in different phases. Proton NMR relaxometry combined with high-resolution magic-angle spinning (MAS) NMR can be exploited to probe physical phase structures, domain sizes, chain conformation and chain dynamics of the final processed material in different phases.

Due to the commercial importance of propylene–ethylene random copolymers (PPR) numerous studies of these polymers have been undertaken in order to characterize their chemical structure, morphology, mechanical, physical and thermal properties [24,25,30,31]. Most of these studies have focused on PPR's synthesized with metallocene-based catalysts [21,25,30]. This is mainly caused by the practical difficulties of characterizing polymers synthesized via different routes leading to increasing compositional and physical structure heterogeneity, requiring more complex analysis.

The aim of this work is to gain in-depth insight into the chemical and physical structures of polypropylene-based polymers produced using heterogeneous Ziegler–Natta (ZN) catalysis. To be more specific, we investigate the chemical and physical composition of an isotactic polypropylene homopolymer (iPP), three propylene–ethylene random copolymers (PPR) and a heterophasic propylene–ethylene copolymer (IEPC). Polymer microstructure was quantified using solution-state ^{13}C NMR spectroscopy. The effect of the amount of comonomer on phase composition and molecular mobility was studied over a wide temperature range. The phase composition was determined using low-field ^1H NMR relaxometry and wide-angle X-ray scattering (WAXS), while small angle X-ray scattering (SAXS) was used to obtain domain sizes. High-resolution ^1H and ^{13}C solid-state NMR spectroscopy were used to identify different chain microstructures present in the amorphous phase. Finally, the strain-rate dependent yield stress of different samples was measured and is shown to be associated with variations in molecular dynamics in the amorphous phase.

2. Experimental

2.1. Sample characteristics

All polymers were commercial grades produced by Borealis AG via multi-stage liquid bulk and gas phase polymerization process using a fourth-generation Ziegler–Natta type catalyst with a conventional silane external donor. No processing step was performed to select polymer chains with a particular constitution or microstructure. The polypropylene homopolymer, hereafter iPP, was a reactor grade with a pentad isotacticity of 99.3%. The three propylene–ethylene random copolymers, hereafter referred to as PPR4, PPR6 and PPR7 were all produced via a visbreaking process

and had ethylene contents of 4.1, 5.9 and 7.1 mol%, respectively, as determined by liquid-state ^{13}C NMR spectroscopy. The heterophasic propylene–ethylene copolymer, hereafter called IEPC23, had a total ethylene content of 23.4 mol% as determined by NMR. The xylene cold soluble fraction in IEPC23 had a M_w of 492 kg/mol. Sample characteristics are provided in Table 1.

2.2. Experimental details

A detailed description of the experimental conditions for solution and solid-state NMR experiments, SAXS and WAXS experiments and the mechanical testing are provided in the Supporting information.

3. Results and discussions

3.1. Analysis of polymer microstructure by solution-state ^{13}C NMR

For the polypropylene homopolymer no indication of ethylene chain units is observed. Although this statement might appear redundant, industrially, it is common to use ethylene to reactivate ZN catalysts resulting in so-called mini-random copolymers with very low ethylene contents of between 0.1 and 0.3 mol%. Similarly, no indications of regio-irregularity are observed, consistent for ZN catalysis. With no comonomer or regio-defects present, the main microstructure originates from tacticity and end groups. The pentad tacticity distribution of 99.3% is determined from the P $\beta\beta$ signals in the methyl region [32]. This isotacticity is typical for iPP produced by ZN catalysis. From inspection of the methyl region of the NMR spectra, it appears that the distribution of stereo sequences remains approximately the same for all samples taking into account the multiple relatively intense signals arising from ethylene incorporation. As far as the end-groups is concerned, only *n*-propyl and *iso*-butyl chain-ends are observed in significant and approximately equal quantities suggesting standard chain initiation and termination mechanisms common for propylene homopolymerization. With respect to crystallizable sequences the average meso sequence length (MSL) was found to be 126 propene units using the relationship, $\text{MSL} = 5 + 2 \frac{[\text{mmmm}]}{[\text{mmmr}]}$.

For the propylene–ethylene random copolymers PPR4, PPR6, PPR7 and IEPC23 characteristic signals corresponding to the incorporation of ethylene are observed [33]. The ethylene content is quantified based on the method of Wang et al. [34] by integration of multiple signals across the whole range of the ^{13}C [^1H] decoupled NMR spectra (Table 2). The triad comonomer sequence distributions are determined using the method of Kakugo et al. [35]. From the normalized triad concentrations, the ethylene content can be calculated as the sum of the ethylene centered triads (XEX) [27]. Due to the different integrals used and difference sources of systematic error, comonomer contents determined by the method of Wang and Kakugo are commonly not comparable at low comonomer contents. The content of isolated ethylene units

Table 1

Sample characteristics: Ethylene content (*E*), molecular weight characteristics (M_w and M_w/M_n), the amount of rubber content expressed as the xylene cold soluble fraction (XS) – (25 °C ISO 16152), melt flow rate (MFR) – 230 °C/2.16 kg ISO 1133, and flexural modulus (flex).

Sample	E, mole %	M_w , kg/mol	M_w/M_n	XS, wt%	MFR, g/10 min	Flex.,MPa
iPP	0.0	360	5.0	1.2	8	1600
PPR4	4.1	~310	~3.4	3.3	8	1000
PPR6	5.9	~310	~3.4	4.7	8	800
PPR7	7.1	~310	~3.4	6.8	8	605
IEPC23	23.4	365		22.0	6	840

Download English Version:

<https://daneshyari.com/en/article/5181651>

Download Persian Version:

<https://daneshyari.com/article/5181651>

[Daneshyari.com](https://daneshyari.com)