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

Vipin Agarwala, Tim B. van Erp, Luigi Balzano, Markus Gahleitner, Matthew Parkinson, Leon E. Govaert, Victor Litvinov, Arno P.M. Kentgens

Radboud University, Institute for Molecules and Materials (IMM), Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands
Dutch Polymer Institute (DPI), P.O. Box 902, 5650 AX Eindhoven, The Netherlands
Department of Mechanical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
Borealis Polyolefine GmbH, Sankt-Peter-Strasse 25, 4021 Linz, Austria
DSM Resolve, P.O. Box 18, 6160 MD Geleen, The Netherlands
DSM Ahead, P.O. Box 18, 6160 MD Geleen, The Netherlands

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.

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].
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) catalyst. 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 $^1$H NMR relaxometry and wide-angle X-ray scattering (WAXS), while small angle X-ray scattering (SAXS) was used to obtain domain sizes. High-resolution $^1$H 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 $M_n$ 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 Pββ 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 propane units using the relationship, MSL = $5 + 2[mmm][mmmm]$.[mmm].

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 [$^1$H] 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>
<thead>
<tr>
<th>Sample</th>
<th>$E$, mole %</th>
<th>$M_n$, kg/mol</th>
<th>$M_w/M_n$</th>
<th>XS, wt%</th>
<th>MFR, g/10 min</th>
<th>Flex, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPP</td>
<td>0.0</td>
<td>360</td>
<td>5.0</td>
<td>1.2</td>
<td>8</td>
<td>1600</td>
</tr>
<tr>
<td>PPR4</td>
<td>4.1</td>
<td>~310</td>
<td>~3.4</td>
<td>3.3</td>
<td>8</td>
<td>1000</td>
</tr>
<tr>
<td>PPR6</td>
<td>5.9</td>
<td>~310</td>
<td>~3.4</td>
<td>4.7</td>
<td>8</td>
<td>800</td>
</tr>
<tr>
<td>PPR7</td>
<td>7.1</td>
<td>~310</td>
<td>~3.4</td>
<td>6.8</td>
<td>8</td>
<td>605</td>
</tr>
<tr>
<td>IEPC23</td>
<td>23.4</td>
<td>365</td>
<td>22.0</td>
<td>6</td>
<td>6</td>
<td>840</td>
</tr>
</tbody>
</table>

Table 1 Sample characteristics: Ethylene content ($E$), molecular weight characteristics ($M_n$ and $M_w/M_n$), the amount of rubber content expressed as the xylene cold soluble fraction (XS) (~25°C ISO 8615), melt flow rate (MFR) (~230°C,2.16 kg ISO 1133, and flexural modulus (Flex).
(I – “randomness”) is quantified as the relative amount of isolated ethylene sequences (EPE) compared to all ethylene centered triads (EEE, EEP, PEP). The average propylene sequence length, \( n_P \), is calculated from the triads according to the relationship, \( n_P = 1 + 2 \left( \frac{[EE]}{[EP]} \right) \), where the dyads [EE] and [EP] are calculated from the triads using the known relationships. From the triad sequence distribution and the degree of isolated ethylene (I) minor but important differences can be seen between the PPR copolymers and the heterophase IEPC23 sample (Table 2). The relative content of the PEP sequence, which represents isolated ethylene incorporation, shows clear differences in the series of PPR copolymers. With increasing ethylene content a higher amount of isolated ethylene units are observed. However, comparing to the other ethylene centered triads the relative ratio of PEP is similar for PPR6 and PPR7 suggesting the same polymerization statistics. As expected, IEPC23 shows a higher relative amount of PEE and EEE sequences, which is an indication of a higher probability of ethylene block formation. In accordance with this observation, a much lower amount of isolated (I) ethylene incorporation (PEP) is observed.

3.2. Analysis of polymer morphology by in-situ X-ray experiments

WAXS measurements for IPP, PPR4 and PPR7 reveal that, during heating at 5 °C/min, crystallinity decreases gradually with temperature until the onset of melting, where the decrease becomes rather sharp (Fig. 1a). The presence of ethylene as a comonomer clearly affects both the initial crystallinity and the melting behavior of the materials. As expected, samples containing ethylene units (PPR4 and PPR7) exhibit lower crystallinity and melting temperature (\( T_m \)) than the homopolymer (iPP). These effects can be essentially ascribed to shorter length of crystallizable propylene sequences (Table 2) [36]. Under the hypothesis that the ethylene co-units are rejected from the crystalline lattice, the melting point depression (with respect to the equilibrium melting temperature, \( T_{m0} \)) can be predicted by the theory of Flory as \( \left( \frac{1}{T_m} - \frac{1}{T_{m0}} \right) = -R \frac{\Delta H_f}{p} \ln p \), where \( \Delta H_f \) is the enthalpy of fusion per repeating unit, and \( p \) the probability that a randomly selected crystallizable unit is followed by another crystallizable unit (for a truly statistical copolymer, \( p \) is simply the mole fraction of crystallizable units) [37,38]. However, Flory’s theory is not expected to quantitatively describe the melting point depression observed in our experiments because (1) the experimental conditions are far from equilibrium, (2) the co-monomer distribution is not truly random, and (3) the co-monomer may partially be included in the crystalline lattice. When \( T_m \) is defined as the temperature at which the melting rate is the highest, the measured melting point depression can be estimated to be about 2 °C per mole percent of ethylene (Fig. 1b).

The thermal stability of crystals depends on their thickness and the amount of lattice defects, including ethylene incorporation. The homopolymer (iPP), which has the longest crystallizable propylene sequences, exhibits the highest crystal thickness of \( \sim 7 \) nm (\( L_c = L_p \cdot x \)). As shown in Fig. 1c, the average long period \( L_p \) increases

![Table 2](image)

**Table 2** Chain microstructure in polypropylene samples: the mole and weight fractions of ethylene units ([E]), triad distribution, content of isolated ethylene units and the average length of propylene sequences (\( n_P \)).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PPR4</td>
<td>4.1</td>
<td>2.8</td>
<td>90.6</td>
<td>6.1</td>
<td>0.0</td>
<td>2.4</td>
<td>0.5</td>
<td>0.4</td>
<td>3.3</td>
<td>73</td>
</tr>
<tr>
<td>PPR6</td>
<td>5.9</td>
<td>4.0</td>
<td>86.0</td>
<td>7.9</td>
<td>0.2</td>
<td>3.9</td>
<td>1.4</td>
<td>0.6</td>
<td>5.8</td>
<td>67</td>
</tr>
<tr>
<td>PPR7</td>
<td>7.1</td>
<td>4.8</td>
<td>83.3</td>
<td>9.1</td>
<td>0.5</td>
<td>4.5</td>
<td>1.8</td>
<td>0.7</td>
<td>7.0</td>
<td>65</td>
</tr>
<tr>
<td>IEPC23</td>
<td>23.4</td>
<td>17.0</td>
<td>67.9</td>
<td>5.5</td>
<td>3.6</td>
<td>2.9</td>
<td>7.7</td>
<td>12.4</td>
<td>23.0</td>
<td>13</td>
</tr>
</tbody>
</table>

Fig. 1. a) WAXD crystallinity as a function of temperature during sample heating at 5 °C/min. The continuous lines are visual guides. The stars represent the points with the fastest rate of crystallinity change. b) Melting temperature versus ethylene content as depicted by stars in Fig. 1a. c) Long-period determined from SAXS, and d) crystal thickness as a function of temperature during sample heating at 5 °C/min.
upon heating, due to melting and re-crystallization processes that especially affect the smallest and most defective crystals and/or parts of them [39]. In this process, some of the density fluctuations within the crystals at the shorter length scales disappear. At the same time, the average crystal thickness remains essentially unaltered up to about 100 °C, as observed in Fig. 1d. At higher temperature, before the onset of melting, crystals tend to thicken. This effect is especially pronounced in the homopolymer just prior to melting. The thickness of remaining crystals increases up to 8 nm (Fig. 1d). Crystal thickening is clearly less pronounced in the copolymers, which might be due to the higher ethylene content in the interface regions.

3.3. Analysis of polymer morphology by solid-state NMR

3.3.1. 1H NMR spin-lattice relaxation

The proton spin-lattice relaxation time constants (T1) for the five samples are measured as a function of temperature (Fig. 2). The T1 of all the samples decreases as a function of increasing ethylene content, except for IEPC23. A mono-exponential function is sufficient to fit the experimental T1 relaxation data for the homopolymer and the PPR samples at all temperatures, whereas a bi-exponential function is necessary to fit the T1 data of the IEPC23 sample.

For iPP, two main relaxation processes, namely methyl group rotation and main-chain motions dominate the 1H T1 relaxation behavior at different temperatures. Two T1 minima, one at −110 °C and the other one at 90 °C, were observed previously in the temperature range from −200 °C to 160 °C [40]. The 1H T1 minimum at −110 °C was attributed to C2-rotation of the methyl group both in the crystalline and amorphous phases, while the minimum at 90 °C was assigned to α-relaxation process in the amorphous phase, namely dynamic glass transition at a frequency of tens of MHz. In Fig. 2 we observe that around 80 °C, when the α-process becomes the dominant source of the T1 relaxation, the variation in 1H T1 is the smallest between different PPR samples. At ~0 °C, when none of the relaxation process dominates, maximum differences are seen between the 1H T1’s of the PPR copolymers. Upon approaching the α-process minimum, the short and long 1H T1 components of IEPC23 can no longer be distinguished. The bi-exponential nature of the T1 data for the impact polymer results from phase separation of propylene-rich and ethylene-rich chains and/or chain fragments.

The major fraction of IEPC23 has exactly the same T1 as that of the iPP while the minor fraction shows a very short T1, indicative of fast segmental dynamics.

3.3.2. Phase composition as determined by 1H NMR T2 relaxation

Proton NMR is a sensitive and robust method for determining phase composition and molecular mobility in complex multiphase polymers [40–42]. In the case of multiphase systems such as semicrystalline polymers, chain motion in the crystalline- and rigid/glassy amorphous phases is restricted. Therefore, the T2 of these phases is dominated by strong homonuclear proton–proton dipolar couplings and is on the order of 8–20 µs. 1H T2 can vary from hundreds of microseconds to a few milliseconds for rubbery materials and to tens of milliseconds for highly viscous liquids. Besides predicting the number of phases/components, the method is inherently quantitative in nature since the amplitude of the relaxation components of each phase is directly proportional to the number of protons present in that phase. The difference in T2 relaxation time of various components increases as a function of temperature and is largest just before the melting of the sample.

The exact theoretical description of the T2 decay rate and its shape is difficult to predict due to the complex nature of the relaxation and morphological heterogeneities of multi-phase polymers. However, a phenomenological model comprising a linear combination of functions appears to reliably define the experimental data. In this study a linear combination of an Abragamian, Gaussian and two exponential functions (Eq. (1)), is found to uniquely fit the experimental data for all samples over the temperature range from 50 °C to 90 °C. These four relaxation components are identified based on a distinct difference in molecular mobility and are designated in the order of increasing mobility, semi-rigid, soft-amorphous and mobile-amorphous fractions:

\[
A(t) = A_0^{Rigid} \exp \left[ -\left( \frac{t}{T_{1,Rigid}} \right)^2 \right] \frac{\sin \left( \frac{\pi}{T_{1,Rigid}} t \right)}{T_{1,Rigid}} \\
+ A_0^{Semi-Rigid} \exp \left[ -\left( \frac{t}{T_{1,Semi-Rigid}} \right)^2 \right] \\
+ A_0^{Soft-Amorphous} \exp \left[ -\frac{t}{T_{1,Soft-Amorphous}} \right] \\
+ A_0^{Mobile-Amorphous} \exp \left[ -\frac{t}{T_{1,Mobile-Amorphous}} \right]
\]

where the parameter \(T_{1,X}^X\) (where X identifies the phase being rigid, semi-rigid, soft-amorphous and mobile-amorphous) is the mobility factor for different components, \(A_0^X\) is the amplitude of the X component, and parameter ‘a’ is related to second and fourth van Vleck moments for the rigid fraction. The relative fraction of each component of this relaxation model — \(A_0^{Rigid} + A_0^{Semi-Rigid} + A_0^{Soft-Amorphous} + A_0^{Mobile-Amorphous}\) — provides the phase composition (in wt%) of the studied polymers. It should be noted that the terms soft-amorphous and mobile-amorphous are chosen somewhat arbitrarily to underline the difference in mobility in the mobile fractions of the material one of which is highly mobile. Fig. 3 shows an illustrative example of the least square fit (using Eq. (1)), of the 1H T2 experimental data (●) and corresponding residuals for the PPR7 sample at 70 °C. Although the general quality of the fit is good, as judged by the residuals, some deviations are observed at longer decay time (>1 ms). This behavior is caused by large amplitude motions in the mobile amorphous phase as is typical for rubbers. It is shown below that the
mobile-amorphous phase displays rubber-like behavior. The origin of the T2 relaxation in rubbers is complex and, as reported in the literature [43,44], cannot be described by a single exponential function.

Several 1H T2 studies of iPP and PPR have been reported in literature [45–52]. All these studies used different relaxation models, comprising two to five components represented by functions such as Gaussian’s, Weibull, exponential and polynomial. The morphology of semicrystalline polymers is very complex and it is therefore difficult to have a unique model to define relaxation profiles of samples synthesized and processed under different conditions. All relaxation models for deconvolution and fitting of 1H T2 data are empirical in nature. So, the best approach is to adopt a relaxation model with a minimum number of components. The addition of extra components in the data fitting must be experimentally justified.

3.3.3. Phase composition and mobility as a function of temperature

A minimum of four components is necessary to fit the T2 data above ambient temperatures. On lowering the temperature from 90 °C to −20 °C, the minimum number of components required for fitting is sequentially reduced from four to three components, and below room temperature to two components. This is related to the timescale of the motions in each phase as a function of temperature in relation to the timescale of the NMR experiments. For further information concerning the fitting procedure and the adaptation of the relaxation model as a function of temperature the reader is directed to the Supporting Information.

Fig. 4A–D shows the variation in relative concentration of the rigid, semi-rigid, soft and mobile amorphous components while Fig. 4E–F show T2 constants for the soft and mobile amorphous components of the five samples as a function of temperature. The T2Rigid and T2Semirigid are not explicitly reported because these two relaxation components were fitted with Abragamian and Gaussian functions and, therefore, the time constant in both these functions is not representative for the transverse relaxation constant associated with exponential functions. In addition, the variations in “effective” T2Rigid (17–19 μs) and T2Semirigid (23–26 μs) components are minor over a temperature interval of −60 °C to 90 °C.

From Fig. 4, several features are observed. For all materials, the amount of rigid fraction decreases with increasing temperature. The rate of decrease is more prominent at temperatures slightly above the glass temperature (Tg) (between 0 °C and 30 °C) than between 40 °C and 90 °C. Below Tg of the amorphous phase, the mobility of chains in the amorphous phases is frozen on the NMR timescale, and therefore adds to the amount of the rigid fraction which appears to be very similar at low temperature for all samples except the phase segregated IEPC23 (Fig. 4A). A similar behavior is observed for the amount of semi-rigid component in all samples except in the temperature range from 0 to 20 °C, at which the amount of the semi-rigid fraction passes through a maximum (Fig. 4B). The initial increase of the semi-rigid fraction on lowering the temperature is due to decreased motion in the amorphous components, with the two components of the amorphous phase becoming indistinguishable from the semi-rigid fraction at the maxima. This is supported by the fact that T2Soft-Am and T2Mob-Am decrease on lowering the temperature and become approximately equal to T2Semirigid around 0–20 °C (Fig. 4E–F). With a further decrease in temperature the amount of the semi-rigid fraction decreases. Such a decrease is most likely due to a further reduction of mobility making parts of the semi-rigid fraction indistinguishable from the rigid component. The aberrant behavior of the semi-rigid fraction for the IEPC23 results from fitting issues and the reader is referred to the Supporting Information.

The soft-amorphous fraction is initially detected between −10 °C and 10 °C for different samples and steadily grows as a function of temperature (Fig. 4C). The temperature range, in which the soft amorphous fraction appears, is consistent with the Tg value of the amorphous phase obtained from DMTA analysis [53]. The concentration of the soft-amorphous fraction increases on heating and becomes almost constant above 60 °C. The T2Soft-Am
steadily increases over the entire temperature range but in the low temperature range $T_{2}^{\text{Soft-Am}}$ shows deviations from expected behavior (Fig. 4E) because the relative concentration of the soft-amorphous fraction is very small, less than 2% and this introduces problems in accurately fitting $T_{2}^{\text{Soft-Am}}$ relaxation component. The mobile-amorphous fraction is initially observed between 20°C and 50°C for iPP and PPR samples and at –20°C for the IEPC23 sample (Fig. 4D,F). It is interesting to note that the higher the ethylene content, the lower the temperature where the mobile-amorphous phase appears. At the onset temperature for detecting the mobile-amorphous component, $T_{2}^{\text{Mob-Am}}$ is in the range of 120–150 μs and this value steadily increases to several hundreds of μsec for iPP and the PPR samples and up to 1.5 ms for IEPC23 (Fig. 4F). $T_2$ values on the order of 0.5–1.5 ms correspond to NMR line width of less than 1 kHz, indicating fast close to isotropic motions.

### 3.3.3. Evidence for the presence of a rubber-like component

Static proton spectra acquired with a $T_2$ filter of 16 ms selects only the mobile-amorphous component. The $T_2$ filtered $^1$H spectra yields a static proton line width (full width at the half height) of approximately 525 Hz for PPR7 (Fig. 5a). In contrast to the wide-line $^1$H NMR spectrum, the line width of the $T_2$ filtered static proton spectrum does not change upon increasing the temperature from 20°C to 80°C. This implies that due to fast molecular motions dipolar couplings are averaged out and the observed proton line width results largely from dispersion of chemical shifts due to chemical structure heterogeneity, and possibly from residual chemical shift anisotropy or dipolar coupling. Furthermore, the intensity of this component increases with increase in temperature. An array of $T_2$ filtered $^1$H NMR spectra (Fig. 5a) recorded at different MAS spinning frequency show that a modest spinning frequency of 400 Hz is sufficient to resolve three different isotropic proton resonances of PPR7. The same spectrum recorded at 21.1T static magnetic field reveals at least five unique proton resonances (Fig. 5b). Fig. 5c shows a 2D $^1$H-$^13$C $J$-resolved spectrum for the PPR7 sample in the absence of any homonuclear decoupling. The $^1$J values observed in the indirect dimension are the unscaled scalar couplings for the CH$_n$ groups. The doublet from the CH moiety shows the expected 1:1 intensity in the $F_1$ dimension. The intensities of the –CH$_2$ and –CH$_3$ multiplets slightly differ from their expected values of 1:2:1 and 1:3:3:1 in an isotropic medium.

$J$ (scalar) couplings are weak interactions observed in NMR due to the interaction of two nuclei mediated by bonding electrons. This interaction is commonly observed in NMR spectra in solutions, where molecules undergo an isotropic tumbling motion. In NMR spectra of polymers J-couplings can be observed when the molecules undergo rapid nearly isotropic motions as is the case in rubbers, e.g., natural rubber [54]. In rigid solids this interaction can only be observed under multi-pulse decoupling conditions. Even for adamantane (a globular molecule with 17 ps correlation time of molecular tumbling) it is not possible to observe $^1$J$_{H-C}$ couplings at modest spinning frequencies [55]. High-resolution proton spectra and resolved scalar couplings at modest MAS frequency point to large amplitude chain motions only observed in polymers.
exhibiting fast, near isotropic chain mobility such as, e.g., butadiene chains in styrene-butadiene rubbers [56]. Thus, these independent experiments confirm the presence of a rubber-like fraction in the amorphous phase of the PPR samples. To the best of our knowledge the presence of a rubber-like fraction in PPR samples with very low ethylene content has never been directly observed before, although it has been suggested previously [52]. This raises an interesting question about the origin and chemical structure of this mobile amorphous fraction in PPR. For the impact copolymers, such as IEPC23, the existence of a separate ethylene-rich rubbery phase is well-known and has been confirmed by various methods (see e.g., TEM pictures of IEPC23 in the Supporting Information). We show further (Section 3.3.6) that ethylene-rich domains populate the mobile-amorphous component in PPR.

### 3.3.5. Effect of ethylene concentration on the morphology and dynamics of the amorphous phase

The concentration and mobility ($T_2$) of both amorphous fractions in PPR increase with increasing ethylene content except for IEPC23 (Fig. 6). Despite the high concentration of ethylene units in IEPC23, the fraction of the soft amorphous phase in IEPC23 is the lowest of all samples due to the good phase separation of chain segments rich in iPP from the chains populated by ethylene units. As a function of temperature, the growth in concentration of the mobile-amorphous component in PPR. For the impact copolymers, such as IEPC23, the existence of a separate ethylene-rich rubbery phase is well-known and has been confirmed by various methods (see e.g., TEM pictures of IEPC23 in the Supporting Information). We show further (Section 3.3.6) that ethylene-rich domains populate the mobile-amorphous component in PPR.

Unlike IEPC23, the size of these domains in PPR should be so small that they cannot be detected by other techniques. In binary blends of polypropylenes with small quantities of ethylene content, the presence of rubbery domains has been previously reported [26,32,58,59]. The situation is probably very similar in the case of PPR. However, the domain sizes will be smaller than those observed in the binary blends due to a very wide distribution of the defects in PPR chains, which would explain why these domains have never been observed by other methods.

### 3.3.6. Chemical composition of the amorphous phases

The solution-state NMR data discussed above shows that random ethylene insertion gives rise to number of microstructures in PPR’s. The knowledge of the partition of these microstructures in different phases is necessary in order to understand structure-property relation. The chemical composition of the crystalline phase revealed that only a small amount of ethylene units are incorporated into the crystalline phase while majority of the ethylene units are partitioned into the amorphous phase. A recent study of ZN catalyzed i-PP shows that at a temperature of 150 °C all defects are excluded from the crystalline phase while previous studies of the PPR polymers prepared with metallocene catalyst by
Vanderhart and co-worker [60–62] indicate that at room temperature ethylene-rich chain fragments are preferentially reside in the amorphous phase. A detailed analysis of the crystalline component in our samples will be published elsewhere. In the discussion below we will focus on the chemical composition of soft- and mobile amorphous fractions, since the studies by Vanderhart could not provide such information due to the lack of spectral resolution for the amorphous phase.

At a temperature of 50 °C, a $^{13}$C detected 2D $^1$H–$^{13}$C correlation spectrum (Fig. 7) of PPR7 shows unique correlations that were used to identify different microstructures in the amorphous phase. One-bond proton-carbon scalar couplings were used to record the 2D spectrum in the absence of any high-power homonuclear decoupling. The free evolution periods in this experiment ensures that only the amorphous phase is visible in the spectrum. The different resonances in Fig. 7 were assigned based on solution-state NMR assignment [34,35] and use the nomenclature suggested by Carman and Wilkes [29]. The peaks at 46.2, 38.0, 37.7, 33.3, 30.7, 28.4 and 24.7 ppm can be assigned to $S_{aa}$, $S_{ag}$, $S_{ad}$, $T_{dd}$, $T_{bd}$, $T_{bb}$ and $S_{bb}$ respectively. The two peaks at $^{13}$C chemical shifts of 30.3 and 27.7 ppm most likely originate from $S_{gd}$/$S_{dd}$ and $S_{bd}$ units, respectively, while the methyl region shows three peaks at 22.2, 21.3 and 20.5 ppm. Besides the fine structure of the resonances of the methyl groups, a total of nine additional chemical moieties could be identified in the amorphous phase of PPR7. From this analysis, we conclude that the amorphous phase is rich in chains with triad sequence such as PPP, PEP, PPE, EPE, PEE and EEE, i.e. has a relatively high ethylene concentration.

3.3.7. Temperature dependence of the chemical composition of the amorphous phase

From the $T_2$ and chemical shift analysis described above, it appears that chain segments rich in ethylene units have an enhanced mobility compared to propylene-rich chains. This means that random ethylene insertions do not only act as structural defects but also as dynamic defects in PPR chains. In order to substantiate this hypothesis, direct carbon excited $T_2$-filtered $^{13}$C NMR spectra for the amorphous phase of PPR7 were acquired at different temperatures (Fig. 8). The spectrum at 23 °C shows the highest peak intensity for resonances (red dotted lines) associated with chemical moieties due to ethylene insertion. Considering the overall ethylene content, the intensity of peaks due to PP units in the amorphous phase (black lines) is very small compared to peaks of...
the ethylene units. The concentration of this ethylene-rich mobile amorphous fraction increases with increase in temperature (Fig. 4D). At 50 °C, the intensity of the peaks from PP and ethylene units is reversed compared to 23 °C spectrum. The spectra at different temperatures show that while the chemical shifts of the lines assigned to ethylene units do not change over the entire temperature range, whereas the chemical shifts observed for the PP units constantly shift to higher ppm values. The chemical shift of \( e \)CH carbon of PP unit is 26.7 ppm in the crystalline phase and 28.95 ppm in the solution-state. The chemical shifts in the crystalline phase indicate a specific conformation with very little degrees of freedom while a solution-state chemical shift represent the mean conformational state of polymer chains resulting from fast chain dynamics. Therefore, the temperature dependent chemical shift changes indicate an increased degree of freedom for PP-rich chains at higher temperatures. Since the peaks from ethylene defects do not show a shift variation one can conclude that the ethylene-rich units already have a high degree of motional freedom at room temperature. This simple experiment demonstrates that for the amorphous phase the insertion of ethylene units in PP chains should not only be interpreted as structural defects but also as dynamic defects.

3.4. Yield stress as a function of strain-rate for different PPR and the role of chain dynamics

The ultimate aim of the analysis of different phases is to understand the mechanical properties in relation to the molecular structure and dynamics of polymers. The effect of temperature and the concentration of ethylene units on chain mobility in the amorphous phase, as determined by NMR, help in better understanding the mechanical properties of PPR.

The rate and temperature dependence of the yield stress of iPP is illustrated in Fig. 9a. With increasing temperature, a smaller value of the yield stress is observed. A clear change in the rate dependence is displayed within the studied temperature and strain rate range. The change in slope indicates that there are two molecular deformation processes contributing to the yield stress [63]. The yield kinetics of polypropylene can be accurately captured using the Ree-Eyring modification of the original Eyring theory [57,64]. Essentially, this theory assumes that two processes act independently and that their contributions to the stress are additive. These processes can be linked to interlamellar (“crystalline”) slip and interlamellar (“amorphous”) slip [63]. Important is the observation that the relative contribution of the amorphous phase to the yield stress becomes increasingly important at lower temperatures when chain mobility in the amorphous phase decreases. The \(^1\)H NMR \( T_2 \) data (Fig. 3) indicates that below 30 °C chain mobility in the amorphous phase freezes out. Chain dynamics, which is involved in structural reorganizations in the amorphous phase during interlamellar slips, matches the strain rate upon approaching \( T_g \). This is confirmed by the dependence of yield stress on strain rate and temperature. At the same temperature, a higher yield stress is observed at faster deformation rate. At lower temperatures, chain mobility is slower and, consequently, yield stress is larger. At temperatures above 50 °C and studied strain rates, the rate of chain dynamics in the crystalline phase (\( \alpha \)-crystalline relaxation process) facilitates intralamellar slips and the crystalline phase becomes the rate determining factor of the dependence of yield stress at a given strain rate.

Fig. 9b shows the rate dependence of the yield stress at room temperature for the different polypropylenes. Here we observe that with increasing ethylene concentration the relative contribution of
the amorphous phase to the yield stress decreases due to the increase in molecular mobility in the amorphous phase upon insertion of ethylene comonomer units (Fig. 6b). The larger the concentration of the ethylene in the amorphous phase the more mobile chains segments in the amorphous phase are present (Fig. 4). The amorphous phase of PPR7 is more mobile than in PPR4. This observation explains the lowering of yield stress at room temperature with increasing ethylene content due to lower barriers for interlamellar slips.

4. Conclusions

In-depth investigations of the phase composition and the chemical microstructure of the phases have been conducted for five commercial grades of polypropylene-based polymers prepared using heterogeneous ZN catalysis. Solution-state NMR was used to identify and quantify the microstructures present in the polymer chains that are generally consistent with ZN based polymerization. WAXD and SAXS data show a reduction in crystallinity, melting temperature, long-period and crystal thickness with increase in ethylene content. In these samples, the temperature dependent time-domain 1H NMR experiments unambiguously establish the presence of a fourth fraction in addition to the crystalline phase, the crystal-amorphous interface and the soft amorphous fraction. This fourth fraction is observed in all samples at temperatures 20–30 °C above Tg. This fraction has rubber-like dynamic properties and consists of segments/chains rich in ethylene units.

The decrease in yield stress with increasing ethylene content and temperature can be related to the greater mobility of chains in the amorphous phase. More studies placing a greater emphasis on the detailed knowledge of the chain microstructures and their distribution over various phases need to be performed to establish detailed structure-properties relations. Particularly interesting will be such studies performed in-situ under mechanical load or during deformation. Equipment to allow such studies using solid-state NMR is under development in our laboratory.

Acknowledgments

The work described in this paper is part of the Research Program of the Dutch Polymer Institute (DPI), Eindhoven, the Netherlands, project number #710. The authors thank Gerrit Janssen, Hans Janssen, and Jan van Os (Radboud University) for their technical support. We furthermore acknowledge the Netherlands Science Organization NWO for their support of the solid-state NMR facility for advanced materials research.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.12.051.

References