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Microstructure and Morphology of Cycloolefin Copolymers

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ABSTRACT: A series of cycloolefin copolymers (COCs) comprised of ethylene and norbornene units were characterized by NMR, WAXD, and DSC. The investigated compositional range was from 35.6 to 79.0 mol % of norbornene. Materials of norbornene content of less than 50 mol % were found to contain blocks of ethylene units and also sequences of alternating ethylene/norbornene units. In these cases the stereoregularity of the chain was relatively high. Materials of norbornene content of more than 50 mol % were also found to contain alternating sequences but additionally showed components of a more random nature including blocks of norbornene units of varying lengths. The stereoregularity of the chain was relatively low in these cases. Differences in the WAXD of the materials were related to these differences in chemical architecture. All the materials showed one T_g which varied linearly with the composition of the copolymer.

Introduction

Recent progress in metallocene catalysis has led to the development of a new generation of polyolefin materials of remarkably, precisely defined molecular architecture compared to the analogous materials prepared by conventional methods.[1,2] This synthesis route allows preparation of very narrow molecular weight distributions with precise control over tacticity. For instance, among the new materials now available are polyethylenes of carefully defined molecular weight and also polypropylenes of exclusively isotactic isomers. Such precise control over chemical structure results in materials of unusual and potentially extraordinary properties.

An example of a new class of polymers emerging from this technology is that of the cycloolefin copolymers (COCs) which are copolymers of ethylene and norbornene units. The statistics and the stereoselectivity of the norbornene insertion can be controlled by selected use of catalyst systems. For example, Arndt et al.[3,4] showed that the formation of meso or racemic chain conformations in oligo(norbornenes) is dependent upon the choice of catalyst system. Additionally, both COCs of random nature and containing alternating sequences are structural possibilities.[5,6]

Random COCs are usually considered noncrystalline as evidenced by (i) an absence of any discernible melting endotherm in heating in the DSC and (ii) the absence of any light scattering such as would be expected from a crystalline polymer. Arndt and co-workers[6] have reported recently that COCs prepared by alternating copolymerization at incorporation rates of 14−37 mol % of norbornene are completely amorphous, while also reporting some crystallinity at lower and higher incorporation rates, indicating some stereoregularity at such norbornene levels.

Depending upon the copolymer composition, the glass transition temperature can vary anywhere between 0 and an excess of 220 °C. In terms of technological applications these materials may be competitors with polycarbonate and poly(methyl methacrylate) (PMMA) in applications requiring transparent, high-performance plastics with relatively high heat distortion temperatures.[5,7,8]

Despite the work referred to above, the characterization of the microstructure of COCs is still very incomplete. Our study comprises (i) a further investigation into the effect of the monomer ratio on the molecular structure and (ii) an investigation of microstructure via X-ray scattering.

Experimental Section

Materials. COCs of different copolymer compositions, received from Hoechst Celanese, were used. These were prepared according to the methods described in ref 9. The norbornene mole fraction of the appropriate polymers was determined by ^{13}C NMR spectroscopy. Glass transition temperatures, T_g, were determined by DSC using the second heating scans (heating rate 20 °C/min).

Measurements. DSC thermograms were obtained using a Perkin-Elmer DSC 7. Experiments were carried out with 8−15 mg of sample under dry nitrogen. All samples were first heated to 220 °C at a rate of 20 °C/min, held at 220 °C for 2 min, and then cooled at 500 °C/min to 0 °C. They were then scanned from 20 to 320 °C at a rate of 20 °C/min.

NMR spectra were obtained using a Bruker AMX 500 spectrometer operating at 125.77 MHz for ^{13}C with a 10 mm diameter sample for maximum signal-to-noise. The temperature was regulated to 30 °C. Polymers were dissolved in $CDCl_3$, which was used as lock and reference (77.00 ppm versus tetramethylsilane). The quantitative spectra were obtained using a 10 μs 90° pulse with a standard inverse-gated proton decoupling pulse sequence and a relaxation delay of 15 s. Some samples were run with shorter recycle delays of 8−10 s to ensure that 15 s gave equilibrium magnetization for the carbons quantified.

For the wide-angle X-ray diffraction (WAXD) study, compression-molded sheets of the materials were prepared; these were molded at 280 °C for 10 min and cooled to ambient temperature at a rate of 20 °C/min. Diffractometry was carried out using a Siemens D500 instrument in transmission mode with Ni-filtered Cu Kα radiation.

Results

DSC. Figure 1 shows the dependence of T_g of the COCs on norbornene content. The dependence of T_g on

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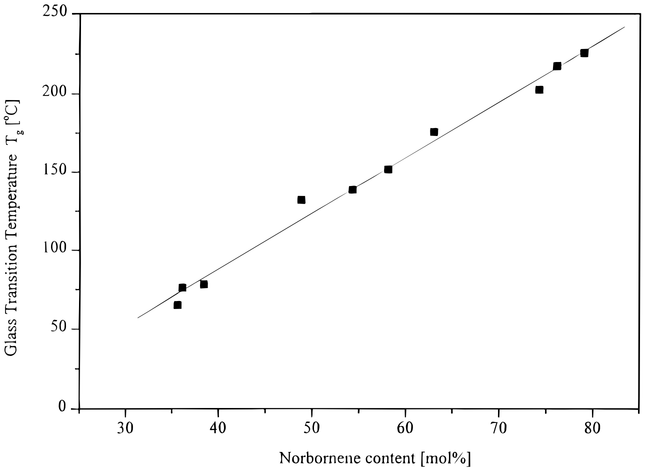

Figure 1. Dependence of glass transition temperature, T_g, upon norbornene content (as determined by DSC).

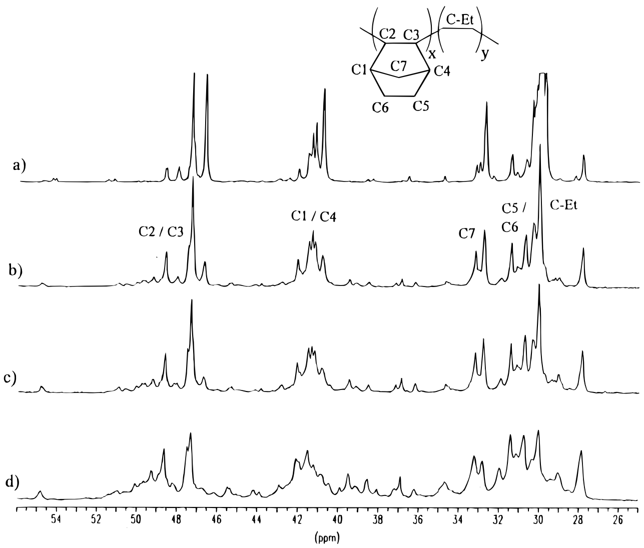

Figure 2. Example ^{13}C NMR spectra of COCs with norbornene contents of (a) 36.1, (b) 58.1, (c) 63.0, and (d) 79.0 mol %.

norbornene content is linear within the investigated composition range of 35−79 mol % of norbornene. This result is in accordance with that of Cherdron et al.[5] Of note is the observation that at a norbornene content of 79% the T_g of 226 °C is slightly higher than the value of 220 °C reported by Haselwander and co-workers for pure poly(norbornene) homopolymer.[10] In contrast to the results of Arndt et al.[6] our DSC scans showed no evidence of melting over the temperature range used (up to 320 °C) in any of the materials available to us.

NMR. Results of ^{13}C NMR investigations of the microstructure of COCs were recently reported by Cherdron et al.[5] and Arndt et al.[11,12]

In ref 5, Cherdron et al. demonstrated the existence of significantly different chemical architectures in random COCs. Our own analysis of ^{13}C NMR spectra confirms this but furthermore shows that the spectra of all observed polymers can be separated into two distinctive patterns (Figure 2).

Pattern 1 was observed for all polymers with a norbornene content of less than 50 mol %. All recorded spectra were very similar in the ^{13}C chemical shift of the signals. As an example Figure 2a depicts the spectrum of the sample with a norbornene content of 36.1 mol %. Because of the random chain architecture each carbon signal is uniquely shifted according to its neighbors along the polymer chain. However, the number of NMR signals of the carbons of this set of COC structures is limited, and all resonances are relatively well separated. This indicates a chemical structure with a limited number of distinct structural units. More details about the chemical architecture of COC chains can be obtained on examination of the signal group at 46−52 ppm. This resonance group can be assigned to C2/C3 methine carbons in the norbornene unit which connects norbornene and ethylene units in the polymer chain. In pattern 1 there appear only two well-separated main resonances in this group at 46.7 and 47.3 ppm. The resonance at 47.3 ppm can be assigned to C2/C3 methine carbons in alternating units along the polymer chain. The signal at 46.7 ppm arises from C2/C3 methine carbons of norbornene bonded to at least two ethylene units. Arndt et al.[12] reported 47.81 ppm for C2/C3 methine carbons bonded in alternating units and 47.28 ppm for C2/C3 methine carbons bonded to longer ethylene sequences, both measured in $C_2D_2Cl_4$ at 100 °C. Since the ^{13}C spectra were quantitative, standard integration of peak areas shows that the fraction of C2/C3 methine carbons bonded in alternating units is approximately 45−50 mol % and the fraction of C2/C3 methine carbons bonded to at least two ethylene units is approximately 35−40 mol %. Only the small signals at 48.05 and 48.64 ppm which contain only 10−15 mol % of all C2/C3 methine carbons arise from blocks of norbornenes.

Our observation indicates that at low norbornene monomer concentrations the insertion of norbornene occurs preferably in alternating units so that the formation of blocks of two or more norbornenes is unlikely. This can be explained by steric effects and is in accordance with the results of Arndt et al.[6] Influences of different catalyst systems in this case are probably low. The resulting structures of COCs of pattern 1 consist mainly of alternating norbornene/ethylene sequences and ethylene sequences of two or more units. Therefore, we conclude that pattern 1 has a high stereoregularity and is mainly characterized by blocks of alternating norbornene ethylene sequences which are connected by longer flexible ethylene units.

In contrast, the observed copolymers with a norbornene content of higher than 50 mol % show a different architecture (pattern 2) (Figure 2b−d). In contrast to pattern 1 the signal groups are broader and less well separated. This is clearest in the spectrum of the polymer with the highest norbornene content (Figure 2d). Each region of resonance is characterized by several signals with small chemical shift differences. This is caused by the chemical shift effects of the varying neighboring carbons and strong configurational effects caused by the linkage of norbornene units in different chiral centers.[3,4] This finding indicates the presence of a more random chain architecture with many different structural segments and a low stereoregularity. The intensity of the resonances depends significantly on the norbornene content. In the spectrum of the material with the lowest norbornene content of pattern 2 (58.1 mol %, Figure 2b), the most intense resonance of C2/C3 methine carbons of the norbornene unit (46−52 ppm) appears still at 47.3 ppm and can be assigned to C2/C3 methine carbons in alternating units of the polymer chain. The quantitative NMR analysis

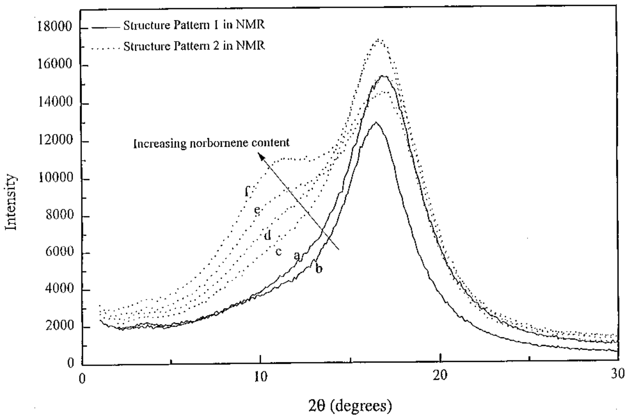

Figure 3. X-ray diffractograms of COCs of copolymer composition (a) 36.1, (b) 48.8, (c) 58.1, (d) 63.0, (e) 74.2, and (f) 79.0 mol %.

shows that this signal represents approximately 50% of all the C2/C3 methine carbons in norbornene units. However, the signal at 46.7 ppm, assigned to C2/C3 methine carbons bonded to at least two ethylene units, corresponds only to approximately 15 mol % of all the C2/C3 methine carbons in norbornene units, i.e., significantly less than the corresponding signal in the spectra of COCs with structure pattern 1. Furthermore, the spectrum shows a broad resonance group between 48 and 52 ppm with a significant peak at 48.6 ppm. This resonance group, which contains approximately 35 mol % of all the C2/C3 methine carbons in norbornene units, can be assigned to C2/C3 methine carbons in blocks of two or more norbornene units. The dominating signal at 48.6 ppm probably can be assigned to C2 methine carbons of blocks of two norbornenes. However, the very broad shape of this resonance group is apparently caused by a high number of shift differences and configurational effects. This finding indicates that structure pattern 2 contains different norbornene blocks of varying length linked in both racemic and meso positions.

With increasing norbornene content the relative intensity of the signals at 47.3 and 46.7 ppm decreases which shows a decrease in the amount of C2/C3 methine carbons bonded in alternating units and bonded to ethylene sequences of at least two units respectively (Figure 2d). In the product with a norbornene content of 79 mol %, the fraction of C2/C3 methine carbons bonded in alternating units can be estimated as approximately 30 mol %. The signal of the C2/C3 methine carbons bonded to ethylene sequences of at least two units disappears almost completely. However, the intensity of the broad signal group between 48 and 52 ppm is more than twice the intensity of C2/C3 methine carbons bonded in alternating units (47.3 ppm).

This result indicates that the chains of polymers with the structure pattern 2 consist mainly of blocks of norbornene units of varying length linked in both racemic and meso positions as well as a certain amount of alternating units. Therefore, the stereoregularity of chains of structure pattern 2 is low. The content of alternating units decreases with increasing norbornene.

WAXD. Diffractograms between 2θ of 2 and 30° of six representative samples are shown in Figure 3. All the scans show a pronounced maximum at $2\theta \sim 17°$, which is independent of copolymer composition. This maximum is far sharper than a normal amorphous halo, having a full width at half-maximum (fwhm) of approximately 5° in the case of the material with 36.1% norbornene content. However, it is emphasized that this is not a true crystalline reflection; it is far too broad, and it is already known that these materials are noncrystalline. Nevertheless, a simple application of Bragg's law indicates a repeat distance of approximately 5.2 Å. With increasing norbornene content, it is clear that a low-angle shoulder develops, becoming a recognizably separate peak at a norbornene content of ~74%. Indeed, careful inspection of the trace from even the sample with the lowest norbornene content shows asymmetry in the higher angle maximum, suggesting some lower angle scatter convoluted with this also.

Our results should be contrasted with those of Arndt et al.,[6] who observed a sharp crystalline reflection at $2\theta \sim 19°$ at norbornene contents above 37 mol % and also reported discernible melting points.

Discussion

From the interpretation of the NMR data above the molecular structures may be separated into two categories depending upon norbornene content:

(a) At low norbornene content, because of steric effects, norbornene insertion occurs preferentially at alternating units. The resulting structure of COCs is characterized by (i) alternating norbornene and ethylene units and (ii) longer ethylene sequences. The stereoregularity of the polymer chains is relatively high.

(b) At high norbornene content two components are in evidence consisting of (i) blocks of norbornene of varying length and (ii) alternating norbornene/ethylene units. Because the insertion of norbornene units occurs in both racemic and meso positions, the stereoregularity of chains is low.

Before discussing our own WAXD results, it is instructive to consider those of Haselwander et al.[10] for amorphous poly(norbornene) homopolymer. These workers found two WAXD peaks located at 2θ ~10° and 19° for this material. Certainly our results show a halo maximizing at ~11° which is particularly associated with materials of high norbornene content (as shown also in ref 6). These materials contain blocks of norbornene/norbornene, and therefore it is suggested that this signal is indicative of norbornene blocks. The increased area under this low-angle peak with increasing norbornene content in materials containing repeating norbornene sequences is consistent with this. Furthermore, the small scattering angle of this halo is consistent with amorphous scatter from a unit of large length scale, such as the norbornene group.

However, the pronounced maximum at $2\theta \sim 17°$ also occurs in materials of low norbornene content which have been shown to contain predominantly ethylene blocks and alternating sequences. Furthermore, the position of this maximum is invariant with content over the entire range studied by us. Thus, we attribute this peak to the component common to all the materials, i.e., the alternating sequences. This is therefore of a fundamentally different origin than the peak at $2\theta \sim 19°$ reported for poly(norbornene) by Haselwander et al.[10]

It should be noted that no evidence for multiple thermal transitions has been found in any of the COCs. In addition, although there is a change in the molecular architecture at about 50 mol % norbornene content, T_g depends linearly on COC content over the range studied. Thus, the presence of different structural features in the various copolymers apparently has no effect on the composition dependence of T_g.

Conclusions

The investigated cycloolefin copolymers show two distinctive chain structures depending on composition. Copolymers with a norbornene content of less than 50 mol % consist mainly of both blocks of alternating norbornene/ethylene sequences and polyethylene sequences. The stereoregularity of polymer chains is relatively high. In contrast, copolymers with a norbornene content higher than 50 mol %, as well as containing blocks of alternating sequences, show a more random component with many different structural features, including repeating blocks of norbornene of varying length. Because the norbornene units can be linked in both racemic and meso positions in such blocks, the stereoregularity of chains in this case is very low.

All the materials show a pronounced WAXD peak at a 2θ of 17°. This is interpreted as arising from blocks of alternating sequences. A wide peak centered on $2\theta \sim 11°$ is most prominent in materials of high norbornene content and is associated with blocks of norbornene units. Further morphological characterization, in particular more detailed characterization of the WAXD signals and small-angle X-ray scattering, is encouraged.

The combination of NMR and X-ray diffraction has been shown to be a very convenient approach for the study of the structure of COCs, correlating chain architecture, as revealed by NMR, and microstructure, as revealed by X-ray diffraction.

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