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Quantitative NMR Spectroscopy and Determination of Polymer Microstructure of Ethylene-Styrene and Ethylene-Isobutylene *Co*-Polymers

*Ruzica Kasalo, Markus Busch**

Summary: Quantitative ^{13}C NMR spectroscopy is used to determine reactivity ratios and end group and branching frequency of ethylene-styrene and ethylene-isobutylene *co*-polymers synthesized at a temperature $T = 205\,^\circ$C and pressure $p = 1650$ bar at different levels of *co*-monomer fraction. In the forefront of the studies quantitative ^{13}C NMR conditions have to be investigated. Optimum conditions are achieved using a relaxation agent Chromium(III) acetylacetonate ($Cr(acac)_3$) at measurement temperature $T = 100\,^\circ$C and a delay time $d_1 = 7$ s with a 90° pulse and inverse-gated decoupling. The analysis of conversion dependence of *co*-monomer content shows an increase in conversion with increasing *co*-monomer content for the ethylene-styrene *co*-polymerization, whereas conversion decreases with rising isobutene fraction in the *co*-polymer. Reactivity ratios for ethylene-styrene as well as for ethylene-isobutylene *co*-polymerization system are determined with values $r_{ES} = 0.09 \pm 0.007$ and $r_{SE} = 2.3 \pm 7.0$ and $r_{EIB} = 3.3 \pm 0.6$ and $r_{IBE} = 6.3 \pm 4.2$. Frequency on methyl end groups, end-of-chain contributions caused by transfer to propionic aldehyde and butyl branches are gained. For the ethylene-styrene *co*-polymer system a decrease in frequency is observed, whereas for the ethylene-isobutylene *co*-polymer system the opposite occurs. Influence of the *co*-monomers on the polymerization reaction steps as transfer to chain transfer agent and back-biting reaction is discussed.

Keywords: ^{13}C NMR; ethylene-isobutylene *co*-polymerization; ethylene-styrene *co*-polymerization; high-pressure radical polymerization

Introduction

In recent years the design of polymers and polymerization processes became an important applied research topic. Focal points are polymer properties and their different applications in everyday life. These properties are determined by polymer microstructure which is controlled by reaction conditions, reactor design and type of polymerization. For instance the synthesis of polymers can be performed by free radical high pressure *homo*- and *co*-polymerization of ethene with a broad range of different *co*-monomers. For the investigation of microstructure and a detail understanding of the correlation of properties and microstructure a broad polymer analysis tool is required. By spectroscopic methods as Nuclear Magnetic Resonance (NMR) *co*-polymer composition, reactivity ratios, characteristic branching structures and branching density can be determined. Ethylene-styrene and -isobutylene *co*-polymers are synthesized by Ziegler-Natta polymerization which result in linear or less branched *co*-polymers.[1–6] With the conventional free radical high-pressure ethylene polymerization branched *co*-polymers with properties caused by the incorporation of the *co*-monomer can be achieved.

Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Petersenstraße 20, 64287 Darmstadt, Germany
E-mail: busch@chemie.tu-darmstadt.de

Experimental Part

Preparation of Polymers

Co-polymerizations have been performed in a continuously stirred tank reactor. The CSTR has a volume of 15 mL and residence times are about 60 s. All experiments have an operational temperature $T = 205\,^\circ\mathrm{C}$ and pressure $p = 1650$ bar. Flow rates of styrene and isobutene are varied from $f_S = 0.002$–0.015 mole/mole and $f_{IB} = 0.02$–0.06 mole/mole. Initiation of the radical *co*-polymerization is achieved by organic peroxides solved in heptane. Propionic aldehyde is used as chain transfer agent.

Preparation of Polymer Samples for NMR Analysis and Quantitative ^{13}C NMR

^{13}C NMR spectra are obtained on a BRUKER DRX 500 MHz spectrometer on 40 wt.- % polymer solutions and 0.05 mol/L Chromium(III) acetylacetonate ($Cr(acac)_3$) in 1,1,2,2 tetrachloroethane-d_4 ($C_2D_2Cl_4$). The spectrometer is run using a 90° pulse τ of 7.7 µs, a spectral width SW of 37 kHz, a relaxation delay d_1 of 7 s, an acquisition time AQ of 0.87 s and inverse-gated decoupling. All spectra are referenced to the solvent at 74 ppm. Details on co-polymer peaks assignments and NMR analysis are found in literature.[2,6,7] Number of branches per 1000 C include methylene groups from the backbone, the *co*-monomer and the branches. The branching frequency has an accuracy of 5% for abundant groups and 30% for butyl branches and methyl groups resulting from chain transfer agent chain ends.

Results and Discussion

Co-polymer composition and the number of end groups and branching frequency were determined by quantitative ^{13}C NMR spectroscopy.

Conversion Dependence

The effect of the incorporation of the two different monomers is shown in Figure 1a and 1b. The course of conversion as a function of styrene mole fraction F_S in the *co*-polymer tends to result in an increase of conversion with increasing styrene insertion. The course of conversion is ambiguous due to the amount of available data. It either passes through a maximum and afterwards declines or it increases and then converges to a certain value of conversion. The isobutene *co*-polymer content F_{IB} decreases with raising conversion. This distinction can be explained with the stability of the co-monomer radicals. A secondary styrene radical is less stable and thus more reactive than a tertiary isobutene radical, which therefore retards the *co*-polymerization rate the higher the isobutene concentration is.

Reactivity Ratios

From the *co*-polymer composition and the mass balance for a CSTR the reactivity

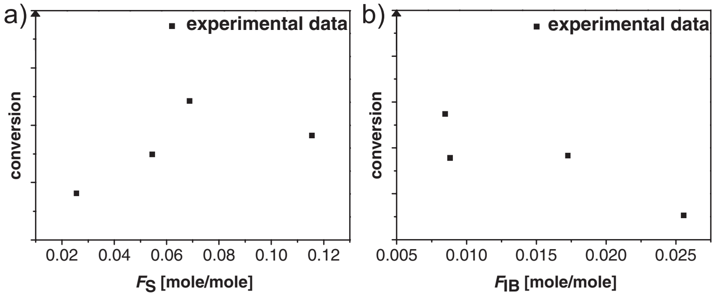

Figure 1.

a: Course of conversion as a function of styrene mole fraction F_S in *co*-polymer. b: Course of conversion as a function of isobutene mole fraction F_{IB} in *co*-polymer.

Table 1.
Reactivity ratios for ethylene-styrene and ethylene-isobutylene free-radical high-pressure *co*-polymerization at $T = 205\,^\circ C$ and $p = 1650$ bar.

co-polymer system	r_1	r_2
ethylene-styrene	2.3 ± 7.0	0.09 ± 0.007
ethylene-isobutylene	6.3 ± 4.2	3.3 ± 0.6

ratios for the *co*-polymer systems were determined. Table 1 presents the reactivity ratios calculated for ethylene-styrene and ethylene-isobutylene *co*-polymerization. By the use of the *co*-polymerization equation in terms of mole fraction (Mayo–Lewis equation), the reactivity ratios of the binary systems can be determined by nonlinear fitting.[8] As *co*-polymer composition is a function of conversion, differential polymerization rates under 5% are achieved for the extend to use the Mayo-Lewis equation. The error for the reactivity ratios given in Table 1 refers to a standard error for parameter estimation which results from nonlinear fitting.

End Groups and Branching Frequency

Figure 2 shows the course of methyl groups (CH_3/1000C) in the *co*-polymer including end groups as a function of styrene *co*-polymer mole fraction F_S. The run of butyl short chain branches (B_4/1000C) and end of chain contributions (EOC(PA)/1000C), caused by transfer to propionic aldehyde, which is used as chain transfer agent, is additionally shown in dependence of resulting *co*-monomer incorporation. For the ethylene-styrene *co*-polymer system the overall methyl groups frequency decreases with increasing *co*-monomer fraction in the *co*-polymer. Thus on the one hand styrene influences transfer to chain transfer agent, which results in less methyl end groups (EOC(PA)/1000C), on the other hand affects backbiting reaction from which butyl branches (B_4/1000C) are formed. A *co*-polymer with a lower number average and higher weight average molecular-weights would be expected, as styrene leads to a decrease in less methyl end groups (PA(EOC)/1000C) and thus longer chains. Precise information gainable from e.g. size exclusion chromatography would help to get more insight to the mechanism of the complex *co*-polymerization reaction steps.

Figure 3 shows a contrary course of the methyl end groups of the ethylene-isobutylene *co*-polymer system. Especially the increase in the overall methyl end groups indicates that isobutene influences transfer

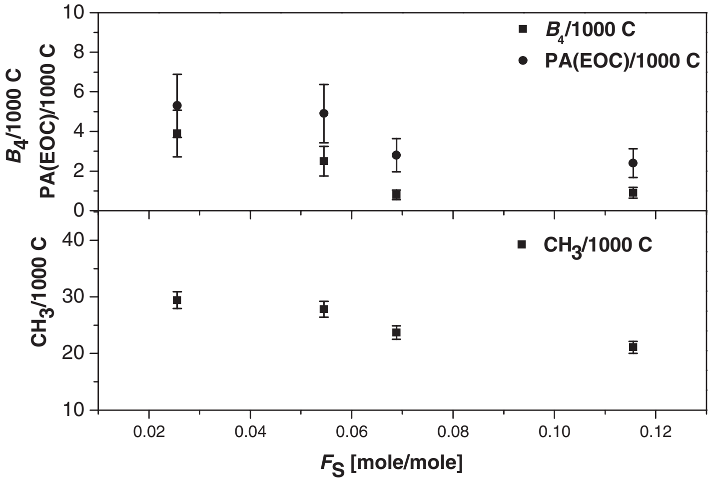

Figure 2.
Course of methyl groups (CH_3/1000C), butyl short chain branches (B_4/1000C) and end of chain contributions caused by transfer to propionic aldehyde (PA(EOC)1000C) as a function of styrene *co*-polymer mole fraction F_S.

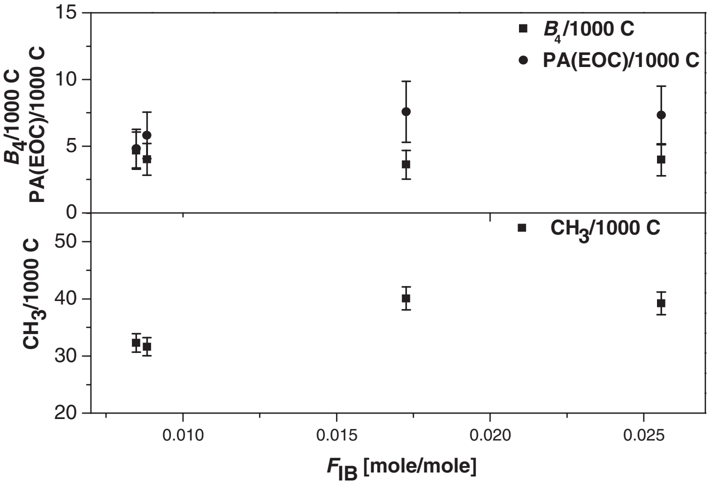

Figure 3.
Course of methyl groups (CH_3/1000C), butyl short chain branches (B_4/1000C) and end of chain contributions caused by transfer to propionic aldehyde (PA(EOC)1000C) as a function of isobutene *co*-polymer mole fraction F_{IB}.

to chain transfer agent either indirectly due to its chemical and steric nature or it directly acts as a chain transfer agent. To assure these observations more data points have to be consulted.

Conclusion

Ethylene-styrene and ethylene-isobutylene *co*-polymers have been identified by ^{13}C NMR techniques with *co*-monomer content in the polymer, type and branching frequency of branches and the overall amount on methyl groups and end groups originating from transfer to chain transfer agent. The study reveals that incorporation of the second monomer has a converse effect on branching frequencies. Reactivity ratios show that the propagation of a styrene monomer with an ethene-terminated macroradical is more favored than the *homo*-propagation of ethene. The propagation of a styrene-terminated macroradicals with ethene is more inhibited due to preferred styrene *homo*-propagation. For the ethylene-isobutylene *co*-polymerization homo-propagation is faster than the cross-propagation.

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