Characterization of Ethylene methyl methacrylate and Ethylene butylacrylate Copolymers with Interactive Liquid Chromatography

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Summary: Copolymers of ethylene with methyl methacrylate (EMMA) and butyl acrylate (EBA), which are of different average chemical composition and block lengths according to NMR analysis, were analyzed by size exclusion chromatography (SEC), differential scanning calorimetry (DSC), Crystallization Analysis Fractionation (CRYSTAF), and high performance liquid chromatography at high temperature (HT-HPLC). With CRYSTAF and DSC crystallizing fractions were detected only in some samples. HT-HPLC fractionated all the samples irrespective of their crystallinity. Homopolymers, PMMA and PE were also found in the copolymer samples of EMMA. EMMA and EBA were separated in HPLC according to the content of polar comonomer. A linear correlation between the MMA content and elution volume could not be established due to the presence of homopolymers as admixtures. In such a case the average chemical composition obtained by NMR does not correspond to the real chemical composition of the copolymers. Unlike EMMA the EBA samples eluted in single peaks, which was used for evaluation of their chemical composition distribution. The comparison of results obtained by fractionation via CRYSTAF and HT-HPLC clearly demonstrates the advantages of the chromatographic approach to study the chemical heterogeneity of olefin based copolymers.

Keywords: ethylene-butyl acrylate copolymers; ethylene-methyl methacrylate copolymers; high temperature-high performance liquid chromatography (HT-HPLC)

Introduction

A large portfolio of polymerization techniques such as catalytic[1–6] and radical polymerization[7,8] has been established to synthesize copolymers from ethylene and polar comonomers such as vinyl acetate, butyl acrylate or methyl methacrylate. The particular challenge of polymerization lies in the control of the distributions of monomer sequences, molar mass (MMD) and chemical composition (CCD). Knowledge of these distributions and their interrelations, which is referred to as molecular heterogeneity, is crucial to elaborate structure-property relationships. The primary analytical technique to determine the MMD is size exclusion chromatography (SEC).[9] The CCD of polyolefins and functionalized polyolefins is routinely analyzed using Temperature Rising Elution Fractionation (TREF), Crystallization Analysis Fractionation (CRYSTAF)[10–14] or DSC.[15] SEC coupled to FTIR[16–21] delivers information about the distribution of comonomer units along the molar mass axis. TREF and CRYSTAF are based on the crystallization of macromolecules from a hot solution. Ethylene copolymers are fractionated according to differences in the crystallizability

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of their ethylene sequences in the polymer chains, i.e., the longest ethylene sequence crystallizes first at higher temperature.[14] Nevertheless random copolymers with a comonomer content above 15 mol% are totally amorphous and therefore cannot be fractionated by TREF or CRYSTAF.

Interactive liquid chromatography presents an alternative to fractionate polymer samples according to their chemical heterogeneity. Here the separation is based on interaction between the polymer molecules and the stationary phase. Besides the possibility to analyze amorphous and semi crystalline samples selective chromatographic modes for particular structural features in the macromolecule like endgroups, block structures or chemical composition can be applied. Numerous examples for the determination of the CCD, the block length distribution of block copolymers and polymer blends using HPLC are described in literature.[22–29] However, all these applications were limited to polymers which are soluble at temperatures between 15-80 °C. Polyethylenes as well as many copolymers of ethylene and polar monomers, which require higher temperatures for their dissolution due to their semicrystalline nature, can not be analyzed by LC-techniques at those temperatures.

Only recently the first systems of interactive liquid chromatography for semicrystalline copolymers of ethylene and polar comonomers at high temperature were published by the research group at DKI in Darmstadt. Liquid chromatography under critical conditions (LCCC) for poly methyl methacrylate (PMMA) at 140 °C was used to separate blends of PMMA and polyethylene (PE) and to analyze ethylene and methyl methacrylate block copolymers.[30] Random ethylene-vinyl acetate, ethylene-methyl acrylate and ethylene-butyl acrylate copolymers were separated according to their chemical composition in gradients of 1,2,4-trichlorobenzene (TCB) → cyclohexanone, decalin → cyclohexanone or decalin → dibenzylether.[31–33] These separations are based on full adsorption and subsequent desorption of the polar comonomer by the gradient. In this paper the characterization of the CCD of ethylene-methyl methacrylate and ethylene-butyl acrylate copolymers by HT-HPLC is described. The results from HPLC are compared with the data obtained from NMR, CRYSTAF, DSC, and SEC.

Experimental Part

High-Temperature Interactive Liquid Chromatography

Measurements were executed using a high-temperature gradient HPLC system PL XT-220 (Polymer Laboratories, Varian Inc, Church Stretton, England). Dissolution and injection of samples were performed using a robotic sample handling system PL-XTR (Polymer Laboratories). The temperature of the sample block, injection needle, injection port and the transfer line between the autosampler and the column compartment was set at 140 °C. Unmodified silica gel was used as the column packing (Perfectsil 300, column 25 x 0.46 cm I.D., particle diameter 10 μm, MZ Analysentechnik, Mainz, Germany). The mobile phase flow rate was 1 mL/min. The polymers were dissolved for 2 hours in TCB at a concentration of 1–2 mg/mL and a temperature of 140 °C. 100 μL of the dissolved polymer sample were injected. The column outlet was connected to an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories). The ELSD was run at a nebulization temperature of 160 °C, an evaporation temperature of 270 °C and with an air flow of 1.5 L/min.

1,2,4-trichlorobenzene (TCB), 1,2-dichlorobenzene (ODCB), decalin and cyclohexanone, all of synthetic quality were obtained from Merck, Darmstadt, Germany. WinGPC-Software (Polymer Standards Service GmbH, Mainz, Germany) was used for data collection and processing.

High-Temperature Size Exclusion Chromatography

A high temperature chromatograph PL 220 (Polymer Laboratories, Varian Inc, Church Stretton, England) was used to determine the molar mass distribution. The temperature of the injection sample block and of the column compartment was set at 140 °C. The flow rate of the mobile phase was 1 mL/min. The copolymers were dissolved for 2 h in TCB (containing 2 g/L butylated hydroxytoluene as antioxidant) at a concentration of 1 mg/mL at 140 °C. 200 μL of the polymer solution were injected. Polystyrene standards (Polymer Standards Service GmbH, Mainz, Germany) were used for calibration of a column set (3 columns Olexis, 25 x 0.8 cm, particle size 10 μm, Polymer Laboratories, Varian Inc, Church Stretton, England).

CRYSTAF

A CRYSTAF apparatus (model 200, PolymerChar, Valencia, Spain) was used for the fractionations at a cooling rate of 0.1 K min^{-1}. 20 mg of the sample was dissolved in 40 mL 1,2-dichlorobenzene. An IR detector monitoring the absorption of the C-H stretching vibration was used.

Differential Scanning Calorimetry (DSC)

The thermal behaviour of the sample was investigated using a DSC 822 from Mettler Toledo (Gießen, Germany). 3-7 mg of the sample were placed in an aluminium pan which was later crimped shut. The following temperature profile was applied: The sample was heated to 150 °C and held isothermal for 2 minutes in order to remove any thermal history. The sample was then cooled to 25 °C at 10 °C/min and held at 25 °C for 2 minutes. Finally, the sample was heated to 150 °C at 10 °C/min heating rate. The cooling and second heating curves were recorded. The melting peak temperature (T_{mp}) and heat of fusion (H_f) values were taken from the second heating curves.

Polymer Samples

All polymer samples were synthesized in the Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), CPP team, Lyon. Samples of polyethylene (PE), polymethyl methacrylate (PMMA) were prepared respectively by transition metal-mediated catalytic polymerization[34] and conventional free radical polymerization using AIBN as initiator. Random copolymers of ethylene-methyl methacrylate (EMMA) and ethylene-butyl acrylate (EBA) copolymers were synthesized by conventional free radical polymerization and multiblock copolymers by metal-modified free radical polymerization using AIBN as initiator (general conditions for polymerization in polar monomer solution in toluene or in bulk; ethylene pressure: 20-250 bar / T = 70 °C). Copolymer samples were classified on the basis of ^{13}C NMR analysis into 3 different categories: two types of randomly distributed ethylene units, namely 1) isolated ethylene units (IE) and 2) short sequences of the ethylene units (SE) and 3) multiblock samples, i.e., with long sequences of the ethylene or polar monomer units. The compositional data given by the producer (from ^1H NMR) and the average molar mass of samples obtained by SEC using a polystyrene calibration are summarized in Table 1.

Results and Discussion

EMMA Copolymer Samples

CRYSTAF was introduced into polymer fractionation in the 1990 s. It separates semicrystalline polymers according to their crystallizability which in turn is related to the chemical composition and the microstructure. The solution of the sample is cooled according to a given programme while the concentration of the sample in solution is being monitored. As a result a profile of concentration (W [%]) vs. temperature is obtained and the first derivative of this profile (dW/dT) gives information about the chemical composition distribution (CCD). Long ethylene sequences (LES) generally crystallize at higher temperatures. An overlay of the first

Table 1.
Microstructure, comonomer content (MMA or BA), weight average molar mass (M_w), and dispersity, D, of the samples.

Sample No.	Microstructure (NMR)	MMA or BA [mol %](NMR)	M_w [kg mol^{-1}]	D
EMMA copolymers				
1	random	94	57.9	1.7
2	(IE)	90	47.6	1.8
3		79	14.4	1.4
4		74	14.9	1.5
5		74	17.3	1.4
6		76	15.9	1.4
7		93	124.3	5.6
8		87	138.1	5.0
9	random	88	435.8	4.4
10	(SE)	63	31.2	2.6
11		51	13.5	1.8
12		77	64.1	4.2
13		82	80.4	4.4
14		87	143.1	5.0
15		91	146.4	4.7
16		74	23.5	1.6
17		68	21.0	1.7
18	multiblock	60	87.5	3.4
19		64	138.0	4.1
20		58	64.5	1.8
21		1	59.0	2.0
22		6	87.7	2.2
23		11	87.8	3.6
24		6	86.3	2.3
25		50	27.1	1.4
EBA copolymers				
26	random	76	75.5	2.9
27	(IE)	93	68.2	2.7
28		87	54.9	1.9
29	random	55	59.5	2.0
30	(SE)	45	40.8	2.2
31		40	75.1	2.5
32		77	158	5.7
33		51	67.8	2.5
34	multiblock	86	279.2	1.8
35		51	267.5	3.6
36		75	37.4	2.3

derivatives of the concentration profiles is shown in Figure 1.

Crystallization peaks were observed only for multiblock samples indicating that they have sufficiently long ethylene sequences to crystallize. However, samples 18, 19 and 25 did not crystallize at all. Among the samples containing a crystallizing fraction, samples 20 and 21 have monomodal peaks and samples No. 22 – 24 have bimodal peaks, with one fraction crystallizing above 80 °C. This indicates that these samples are chemically inhomogeneous and may contain fractions with a different chemical composition or micro-

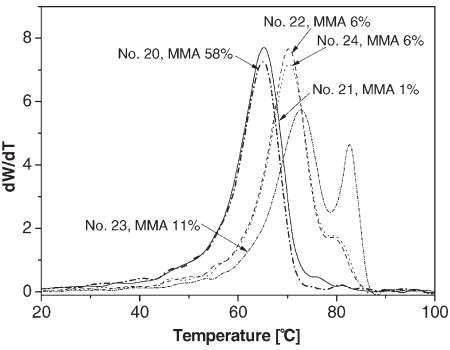

Figure 1.
Overlay of curves obtained by CRYSTAF for EMMA samples.

structure. It is surprising that samples No. 20 and 21 show crystallization peaks at the same temperature even though they have very different contents of MMA (58 and 1 mol % respectively). Copolymers with IE and SE random microstructure (samples 1-17) turned out to be completely amorphous, i.e., CRYSTAF analysis only yielded a soluble fraction.

DSC separates a given sample with respect to its crystallizability from the melt and therefore complements the CRYSTAF results. An overlay of second DSC-heating curves of multiblock copolymer samples is shown in Figure 2.

Melting was only observed for multiblock samples, except for sample 25 which confirms the results from CRYSTAF, i.e. only these samples contain crystallizable portions. High MMA content, according to NMR average chemical composition, in samples No. 18 – 20 suggests they could be amorphous materials. However, their DSC responses show the presence of crystallizing fractions. Although CRYSTAF analysis indicates the presence of at least two chemically different components in some samples (22, 23, and 24), DSC does not confirm this finding as the same samples only showed a single broad melting endotherm. Second heating curves of DSC did not show any trend. The samples No. 20 and 21 show almost identical behavior in spite of the large difference in their MMA contents (58 contra 1 mol % MMA). The reason for this unexpected observation was later revealed from HPLC data.

By separating with regard to hydrodynamic volume in solution, SEC yields information on the molar mass heterogeneity and dispersity of the samples. The EMMA samples differ substantially in their average molar mass (M_w) as well as in their molar mass distribution (Table 1). Moreover, some samples exhibit bimodality (Figure 3).

The hydrodynamic volume is a function of both molar mass and chemical composition, i.e., bimodality therefore could be an indication of the presence of chemical or molar mass heterogeneity. Using the experimental set-up with refractive index (RI) detector, no information on the chemical composition of the different molar mass fractions can be obtained. This could be retrieved from SEC-FTIR. But, as the eluting peaks are not baseline separated, HPLC could be more promising here.

As a starting point for the HPLC analysis a method developed by Albrecht et al.[31], for the separation of EMA copolymers according to their chemical composition, was chosen. This method uses a gradient of decalin → cyclohexanone as mobile phase and unmodified silica gel as stationary phase at 140 °C. As acrylate units are polar in nature, they will selectively

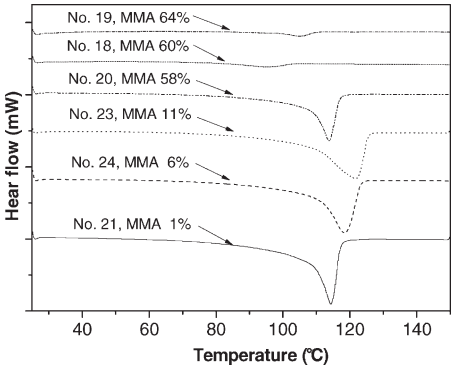

Figure 2.
Overlay of DSC second heating curves of EMMA samples.

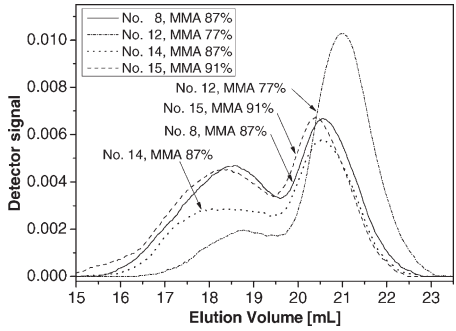

Figure 3.
Overlay of the chromatograms of EMMA copolymer samples, as obtained by SEC.

interact with a polar stationary phase while the non-polar ethylene units do not contribute to the retention. Thus elution is based on the content of the polar comonomer. Solubility experiments showed that some samples did not dissolve in decalin. Therefore, TCB was chosen instead of decalin. Samples were dissolved in TCB at 140 °C and 100 μL of each sample were injected. A linear gradient starting with 100% solvent A (TCB) for 5 min was used. Solvent B (cyclohexanone) reaches 100% after 20 minutes. The elugrams are shown in Figure 4. The copolymer samples elute with different elution volumes, but they were not sufficiently separated.

To improve the resolution the gradient was modified and pure cyclohexanone was replaced by a mixture of cyclohexanone/ TCB 80/20 v/v as solvent B. The volume fraction of solvent B was increased linearly to 60% within 10 minutes and then increased to 100% in 15 min. It was held at 100% for 5 min and finally the initial chromatographic conditions were re-established. As Figure 5 shows the modified gradient enabled to obtain, in the majority of cases, base-line separation of the components.

The majority of the samples elutes in multimodal peaks, some in one peak. The peak with the smaller elution volume is identical or close to the elution volume of the PE standard (Figure 5b) and the peaks with the largest elution volume appear close to the elution volume of PMMA (Figure 5a,b). These results suggest that those samples could be blends of the homopolymers and the copolymers. CRYSTAF and DSC peaks of sample No. 20 (58 mol % MMA) and DSC peak of sample No. 18 (60 mol % MMA) shown in Figure 1 and 2 support this assumption, due to their crystallization even at high mol% of comonomers. Moreover the same samples elute in more than one peak in chromatography (Figure 5b). From this it can be assumed that the same crystallization behavior for sample No. 20 and 21 in CRYSTAF and DSC could be possibly due to the presence of PE homopolymer in sample No. 20. Information about the presence of homopolymers cannot be obtained by NMR, since it gives only

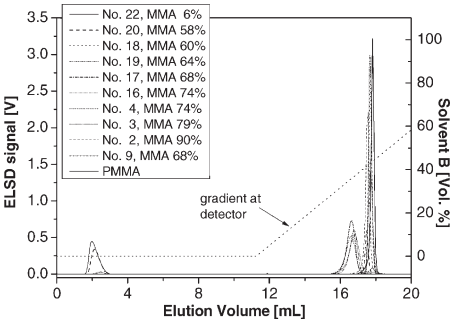

Figure 4.
Overlay of the chromatograms of EMMA copolymer samples. Stationary phase: Perfectsil 300. Mobile phase: TCB and gradient TCB → cyclohexanone. Temperature: 140 °C. Notice: The gradient at the ELSD is indicated in dotted line.

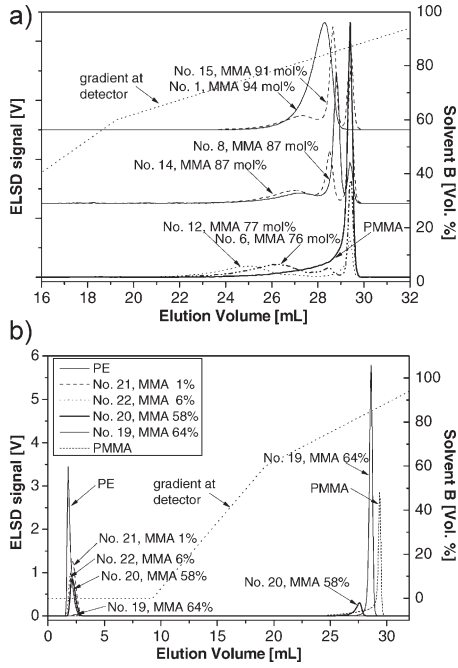

Figure 5.
Overlay of chromatograms of EMMA samples: a) with isolated ethylene units and short ethylene sequences b) multiblock copolymer samples. Stationary phase: Perfectsil 300. Mobile phase: TCB and gradient TCB → cyclohexanone/ TCB (80/20 v/v). Temperature: 140 °C. Gradient at the ELSD is indicated by a dotted line.

average chemical composition. As a result the average chemical composition obtained from NMR (Table 1) is not identical with the actual average chemical composition of the copolymer present in these samples. Consequently the elution volume of the samples cannot be correlated with the average chemical composition. We emphasize that the detection of the presence of homopolymers in mixture of copolymers (especially in the case of multiblock copolymers) is not an easy task. Consideration of peak heights (or areas) of the chromatograms (Figure 5) implies that the copolymers with isolated ethylene units or short ethylene sequences have broadly distributed chemical composition. In a quantitative way the CCD of these comonomers can be determined after elaboration of coupling HPLC to chemoselective FTIR. Such procedures were described in references.[30–33]

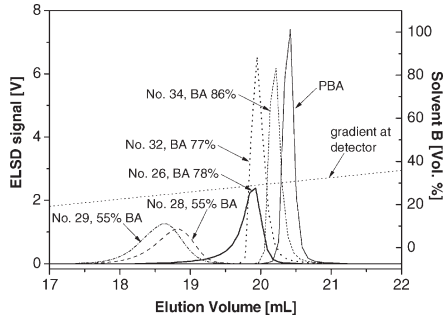

Figure 6.
Overlay of chromatograms of EBA samples. Stationary phase: Perfectsil. Mobile phase: TCB and gradient TCB → cyclohexanone/ TCB, 30/70 vol. %. Temperature: 140 °C. Notice: The gradient at the ELSD is indicated in dotted line.

EBA Copolymer Samples

The EBA samples did not show crystallization in CRYSTAF nor melting in DSC. The same chromatographic system as used for HPLC analysis of EMMA was used to separate butyl acrylate copolymers. However, as butyl acrylate is less polar than MMA, the composition of solvent B was further modified and cyclohexanone/TCB 30/70 v/v was used instead of cyclohexanone/TCB 80/20 v/v. An overlay of chromatograms of selected EBA samples is shown in Figure 6.

All EBA samples eluted in single peaks, i.e., without homopolymers as admixtures. The elution volume increases with increasing butyl acrylate content in the copolymer samples. The average composition obtained from NMR (Table 1) correlates with the elution volume at the peak maximum as illustrated in Figure 7.

The scattering of the data points around the line in Figure 7 probably is caused by different factors. One factor is that the average composition determined by NMR is not necessarily the composition at the peak maximum (i.e., values of the elution volume shown in Figure 7), especially if the shape of CCD is not symmetrical (for example, sample 26 or 32 in Figure 6). Another factor is that the signal of the ELSD detector depends on the composition of the eluent[31] and eventually also on the copolymer composition. For chemically narrow distributed copolymers this error is relatively small, in the case of broadly distributed copolymers this may cause an error in the determination of the peak maximum. As a third reason the microstructure (block length) of the macromolecules has to be considered. Thus it can be expected that the elution behaviour of a block copolymer differs from that of

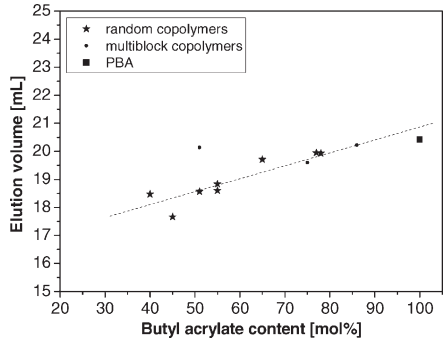

Figure 7.
Relationship between the elution volume and the average polar comonomer content of EBA copolymer samples.

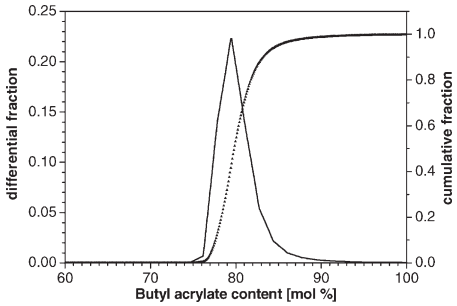

Figure 8.
Differential (solid line) and cumulative (triangles) BA distributions in mol % of sample No. 32.

a random copolymer with identical comonomer content. Unfortunately, the small number of the EBA samples with defined structure does not allow demonstrating this effect clearly. In general, the elution volumes of the EBA copolymers correlate linearly with the average chemical composition. Such a trend has been observed for other ethylene/acrylate copolymers also by Albrecht et al.[32,33] Using the line shown in Figure 7 as a calibration curve for the random EBA copolymers, the differential and cumulative distributions of the percent of BA for EBA copolymer sample No. 32 is shown in Figure 8. In contrast to DSC or CRYSTAF, CCD is obtained for both amorphous and semicrystalline samples and as well as for the copolymer alone or with a blend by HPLC.

Conclusion

Samples prepared by copolymerization of ethylene with MMA or BA were characterized by NMR, SEC, DSC, CRYSTAF and HT-HPLC. While DSC and CRYSTAF were able to detect crystallizing fractions only in EMMA copolymers with both multiblock structure and low MMA content, DSC and CRYSTAF did not show any crystallizing fractions in EBA copolymers. On the other hand, high temperature gradient HPLC based on adsorption and desorption of the polymers allowed to fractionate all EMMA and EBA samples according to their polarity, irrespective of their crystallinity. HPLC separation enabled to separate and detect homopolymers of methyl methacrylate and/or ethylene, which were present as admixtures in the EMMA samples. The presence of these homopolymers in the samples misleads the average chemical composition of the real copolymers obtained by NMR. Unlike EMMA samples, EBA copolymers eluted in single peaks, i.e., without admixtures. An overall comparison of the elution volumes of the copolymer samples showed that they were fractionated according to the concentration of the polar comonomer in both EMMA and EBA copolymers. Using the linear correlation between the average comonomer content (obtained by NMR) and the elution volume enabled evaluation of the chemical composition distribution for random EBA samples. As illustrated in this paper, HPLC enables to separate homopolymers from copolymers even in cases where CRYSTAF or DSC fails and it requires much less time and solvents than CRYSTAF. Moreover, HPLC analysis enables to check, if the average chemical composition obtained by the NMR spectroscopy corresponds to the copolymer alone or to blends of both copolymer and homopolymer(s) or eventually to a mixture of both homopolymers. Thus polymer chemists may greatly benefit from application of HPLC in the characterization of new polymer samples.

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