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# Detection and quantification of branching in polyacrylates by size-exclusion chromatography (SEC) and melt-state $^{13}$C NMR spectroscopy

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ABSTRACT

Chain branching has been investigated in a homologous series of poly(*n*-alkyl acrylates) (methyl, ethyl, *n*-butyl, *n*-hexyl) obtained by radical polymerization. The total amount of chain branching was quantified using melt-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. It gave access to low degrees of branching in both soluble and insoluble polyacrylates, homopolymers and copolymers. The lowest degree of branching was found for the ethyl member of the series with quantification by conventional solution-state NMR found to take a prohibitively long time. The method proposed here is compared to the ones published previously, and previous literature results are critically reviewed.
The presence of long-chain branching (LCB) was selectively detected using multiple-detection size-exclusion chromatography (SEC), with LCB being found for all soluble homopolymers but the poly(*n*-butyl acrylate). This finding was confirmed by close examination of the Mark–Houwink parameters for the various polyacrylates studied in this work or those previously published.

## 1. Introduction

Polymer chain branching is present in many important polymers such as polyethylene, polyacrylics and starch [1]. For polyethylenes, poly(vinyl acetate) and poly(alkyl acrylates) produced by radical polymerization, one may distinguish between short-chain branching (SCB) – produced by intramolecular transfer to the polymer [2] and long-chain branching (LCB) [3] – produced by intermolecular chain transfer to the polymer [4]. The presence of SCB has an effect on the melting point, glass-transition temperature and hardness as well as the degree of crystallinity in semi-crystalline polymers. In contrast, long-chain branching affects rheological properties such as sedimentation behavior, intrinsic viscosity, and the viscosity and elasticity of polymer melt. Long-chain branching may also directly affect the final application properties such as the adhesive nature of pressure-sensitive adhesives [5–8]. Three key methods are commonly encountered in the literature to determine the degree of branching: $^{13}$C nuclear magnetic resonance (NMR) spectroscopy, multiple-detection size-exclusion chromatography (SEC) and infrared (IR) spectroscopy. Another important method is the application of off-line light scattering performed after fractionation by SEC [9].

The occurrence of branching in poly(alkyl acrylates) has been previously reported by numerous research groups and is well documented in the literature. For poly(*n*-butyl acrylate) branching of up to a few percents of the monomer units were observed by $^{13}$C NMR spectroscopy for systems synthesized by emulsion polymerization [10–17], solution polymerization in cyclohexane [18], pulsed-laser polymerization in bulk, heptane or toluene [2] as well as by nitroxide-mediated controlled radical polymerization in bulk and miniemulsion [19]. Branching was also observed for poly(2-ethylhexyl acrylate) obtained by emulsion polymerization [10,20] or solution polymerization in cyclohexane [21], as well as for poly(methyl acrylate) and poly(ethyl acrylate) obtained by emulsion polymerization [15]. The effects of the intramolecular transfer to polymer leading to SCB on the polymerization kinetics of alkyl acrylates have also been reviewed by the IUPAC working party on ‘modeling of polymerization kinetics and processes’ [22] and explored in detail [23–25]. Specifically, McCord et al. showed that

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hydrogens opposing acrylate side groups are prone to abstraction by backbiting [26] and Chiefari et al. report the synthesis in solution of several polyacrylate macromonomers through propagation, transfer to polymer and β-scission [27]. Zosel and Ley [28] observed that poly(*n*-butyl acrylate) synthesized by emulsion polymerization contained gels and exhibited the viscoelastic behavior of a slightly crosslinked material. Gel formation was also observed in the polymerization of methyl acrylate in solution [29], the polymerization of n-butyl acrylate in bulk [30], in solution [31] and in emulsion [11], the polymerization of 2-ethylhexyl acrylate in emulsion [20] as well as the polymerization of acrylates with long alkyl chains [32,33].

For some polymers, such as polyolefins, the use of $^{13}$C NMR spectroscopy for the quantification of branching is well developed, allowing for discrimination between SCB with lengths up to 6 carbons by their chemical shifts [6,34,35] and in favorable cases longer by solvent effect or nuclear relaxation behavior [36]. The quantification of LCB has also been demonstrated for polyolefins produced with macromonomer incorporation. For poly(alkyl acrylates), however, the NMR spectra are more complex [18,21] and thus only the total degree of branching, i.e. SCB + LCB, may be quantified [18]. In contrast, SEC and rheology are both far more sensitive to LCB [6,37]. Thus in order to fully describe the molecular architecture information from spectroscopic and chromatographic/rheological techniques must be combined [6,38].

For poly(alkyl acrylates) the branching is best quantified using quantitative 1D $^{13}$C NMR methods. This approach has been demonstrated in both the solution-state [16–19,21] and swollen-state [11,20]. Although solution-state NMR is more widely accessible and provides higher spectral resolution it requires the samples to be fully soluble, this can be a problem for poly(alkyl acrylates) particularly those exhibiting a gel fraction [11,20,39]. Thus the full capabilities of quantitative $^{13}$C NMR spectroscopy have not yet been fully explored as both spectral resolution and sensitivity are required. One approach to increase sensitivity is to measure on the bulk polymer using solid-state NMR, however, spectra have low sensitivity and resolution due to lack of motional averaging present in solution and when swollen [40]. To increase sensitivity cross-polarization (CP) may be applied at low temperatures [41–43]. Spectral resolution may be increased by applying magic-angle spinning (MAS) [44], however, the resolution is still much lower than that commonly encountered in solution-state NMR. A further increase in resolution may be achieved by fast-MAS or by swelling the samples and using moderate MAS frequencies. The abbreviation HR-MAS (high-resolution MAS) is often used to designate routine $^{13}$C single-pulse spectra of swollen samples under MAS. Plessis et al. quantified degrees of branching in poly(*n*-alkyl acrylate) and poly(2-ethylhexyl acrylate) using HR-MAS and tetrahydrofuran (THF) as a swelling agent [10,20]. However, for swollen samples long measuring times limit the sensitivity: a minimum measuring time of 28 h was used, which is the shortest measuring time found in literature for quantitative measurements.

Recently, the alternative approach of melt-state MAS NMR has been demonstrated to achieve quantitative high-resolution spectra of bulk polymers. The method combines key aspects of both solution-state and solid-state NMR and was found to be most useful for material which were difficult to dissolve or insoluble, such as polyolefins [34,35,38,45]. Degrees of branching as low as 0.001% of the monomer units could be quantified in one day for sparsely branched polyolefins. The aim of this work is to adapt the quantitative melt-state NMR technique to poly(*n*-alkyl acrylates) homopolymers and poly(alkyl acrylate) copolymers, then to compare its potential to measure reliable degrees of branching to that of other quantitative $^{13}$C NMR methods, and finally to use the most efficient $^{13}$C NMR method to determine reliable degrees of branching on different samples and compare them. The term melt is used here to designate the physical state of an amorphous polymer sample at temperatures far above its glass-transition temperature $T_g$, whether it is crosslinked or not.

For characterization of LCB the poly(*n*-alkyl acrylate) homopolymers were separated and analyzed by multiple-detection SEC. Separation by SEC occurs according to hydrodynamic volume and not molecular weight or degree of branching [46–49]. Polymer chains may have the same hydrodynamic volumes but different molecular weights if LCB is present [49]. This leads to an incomplete separation in terms of molecular weight as chains with different molecular weights but the same hydrodynamic volume will elute at the same time [50]. This effect has only recently been proven significant through multiple-detection SEC analysis of polyacrylates, [3] i.e. determining molecular weights by both universal calibration using an online viscometer and by light scattering. Incomplete separation results in a mixture of chains with a distribution of molecular weights eluting at a given elution time. The number-average molecular weight of this local molecular weight distribution may be obtained through the use of universal calibration using a viscometer, while light-scattering based techniques yield the weight-average molecular weights. This incomplete separation prevents the determination of molecular weight distributions. We previously proposed to circumvent this issue using hydrodynamic volume distributions for comparative studies [51,52]. In this work this incomplete separation is used to detect LCB among polyacrylate homopolymers. Due to the incomplete solubility of the copolymers SEC was only used to investigate the branching topology of the homologous poly(*n*-alkyl acrylates) homopolymers. The polyacrylate materials analysed in this work are randomly-branched polymers, similar to low-density polyethylene (LDPE) produced in a high-pressure process [53], and not mixtures of preformed linear and branched polymer chains [37,54].

## 2. Experimental section

### 2.1. Materials and polymerization

Homopolymers were prepared by conventional radical solution polymerization of *n*-alkyl acrylate monomers (Fig. 1) with the details described elsewhere [55]. The specific homopolymers produced were: poly(methyl acrylate), poly(ethyl acrylate), poly(*n*-butyl acrylate) and poly(*n*-hexyl acrylate), hereafter abbreviated as PMA, PEA, PnBA and PHxA respectively. All homopolymers were found to be atactic by $^{13}$C solution-state NMR (see supporting information).

A poly(2-ethylhexyl acrylate), P2EHA, was synthesized in the same conditions but not further characterized by NMR. A poly(*t*-butyl acrylate), PtBA, was synthesized by pulsed-laser polymerization (PLP) as described in Ref. [56].

Copolymers were provided by ATOFINA S.A. (Cerdato, Serquigny, France) and were obtained by semi-batch (semi-continuous) emulsion copolymerization of the following monomers: 2-ethylhexyl acrylate, methyl acrylate, acrylic acid and a crosslinking comonomer hereafter abbreviated 2EHA, MA, AA and CL respectively (Table 1). The chemical structure of the physical cross-linker is confidential but it may be assumed to form hydrogen bonds with the acrylic acid monomeric units. All copolymers were synthesized at 60 °C except Copo3 which was synthesized at 85 °C. The copolymers are expected to be branched statistical copolymers, with the possibility of higher AA concentration at the ends of the polymer chains and on the surface of the particles (see supporting information for details). As the surfactants used during synthesis may also be observed by NMR, analysis of latex samples containing one anionic and one non-ionic surfactant was performed to allow assignment (see supporting information). It should be noted that

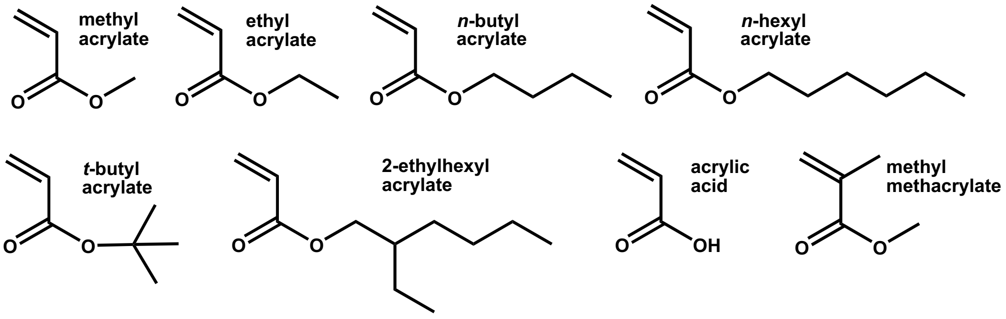

**Fig. 1.** Chemical structures of the acrylic monomers of the investigated polymers.

poly(alkyl acrylates) produced in this manner are known to contain a considerable proportion of high molar mass, highly branched or crosslinked polymer, thus molar mass distributions may only be obtained from the soluble fraction and not the sample as a whole. These materials are not commercial grades, and were specifically synthesized for research purposes, but are similar to commercial pressure-sensitive adhesives.

Materials for SEC analysis have been previously described in Ref. [3].

### 2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out on a TG 50 Mettler device under a nitrogen atmosphere with the temperature increased from room temperature to 900 °C at 10 °C min$^{-1}$. The decomposition temperature (DT) was defined as the temperature at which the sample had lost one percent of its initial mass. Decomposition temperatures are compared to glass-transition temperatures previously determined by differential scanning calorimetry (DSC) at 10 °C min$^{-1}$ [55,57] (Table 2). The large difference in $DT - T_g$ observed between the homopolymers and copolymers is assumed to originate from a degradation of surfactants in the copolymers at a lower temperature than the polymers themselves.

### 2.3. Size-exclusion chromatography (SEC)

The multiple-detection SEC setup using THF as an eluent at 40 °C has been previously described in detail in Ref. [3]. Injections were performed at 6–7 g L$^{-1}$, half the empirical maximum concentration. Recovery was shown to be quantitative by measurement of the apparent recovery using the refractometer for three injections of PnBA (100, 98 and 104%) and two injections of PHxA (103 and 98%). This implies that the homopolymers do not contain any gel within experimental error. The specific refractive index increment in THF was taken as 0.070, 0.071, 0.063, 0.059, 0.064 and 0.073 mL g$^{-1}$ for PMA (see supporting information), PEA [3], PnBA [3], PtBA (see supporting information), PHxA [58] and poly(2-ethylhexyl acrylate) [3] respectively.

The multiple-detection SEC data was analyzed using a combination of the TriSec software (Viscotek) and custom software developed by the authors, the latter designed to minimize the influence of difference in sensitivity of the different detectors [3]. The molecular weight was determined by three methods: universal calibration, triple detection and low-angle laser light scattering.

**Table 1**
Quantitative composition of the polyacrylate copolymers.

| Sample | Composition (wt%) |
|---|---|
| Copo2EHA | 2EHA + AA (1%) |
| Copo1 | 2EHA (80%) + MA (19%) + AA (1%) |
| Copo2 | 2EHA (79.5%) + MA (18.75%) + AA (1%) + CL (0.38%) + MMA (0.38%) |
| Copo3 | 2EHA (79.5%) + MA (18.75%) + AA (1%) + CL (0.38%) + MMA (0.38%) |

### 2.4. Solution-state NMR

Solution-state NMR spectroscopy was undertaken on a Bruker DRX500 spectrometer (Bruker BioSpin, Germany) operating at a $^{13}$C Larmor frequency of 125.76 MHz. For the homopolymers, solutions of ca 300 g L$^{-1}$ in $CDCl_3$ were used and spectra recorded at temperatures between 29 and 33 °C using 19 500–21 000 transients. For the copolymer Copo2EHA a polymer solution of <20 g L$^{-1}$ in $C_2D_2Cl_4$ was used (the sample did not visually fully dissolve even after several days under stirring at high temperature, suggesting a significant gel content) and spectra recorded at a temperature of 100 °C using 19 808 and 20 267 transients. Quantitative $^{13}$C spectra were recorded using single-pulse excitation, using a 6.70 μs 90° pulse, inverse gated waltz16 decoupling and a relaxation delay of 10 s. Apodization was achieved using an exponential window function equivalent to a linewidth of 5 Hz. The $^{13}$C chemical shift scale was indirectly referenced to tetramethylsilane (TMS) at 0.0 ppm by setting the central resonance of $CDCl_3$ to 77.0 ppm.

### 2.5. Swollen-state NMR

Swollen-state NMR spectroscopy was undertaken on a Bruker DRX500 spectrometer (Bruker BioSpin, Germany) operating at a $^{13}$C Larmor frequency of 125.76 MHz using a 4 mm solid-state MAS NMR probehead. A MAS rotational frequency of 5 kHz was chosen to limit the presence of spinning sideband within the spectral regions of interest. The copolymer Copo3 was swollen by approximately 50% volume in THF-$d_4$ and spectra recorded at room temperature using 2096 transients. To insure quantitative spectra the $^{13}$C $T_1$ relaxation time were measured via the saturation recovery method, with $^{C}T_1$ for all sites (except carbonyl) found to range between 0.2 and 1.0 s. Quantitative $^{13}$C spectra were recorded using single-pulse excitation, with a 4.0 μs 90° pulse, inverse gated continuous wave decoupling (50 kHz) and a relaxation delay of 5 s. The acquisition time of the FID was optimized to 102 ms, as

**Table 2**
Decomposition temperatures (*DT*) and glass-transition temperatures $T_g$ measured by TGA and DSC respectively. Difference between $T_g$ and *DT* indicated in brackets.

| Sample | PMA | PEA | PnBA | PHxA | Copo2EHA | Copo1 | Copo2 | Copo3 |
|---|---|---|---|---|---|---|---|---|
| DT (°C) | 227<br>(+206) | 234<br>(+248) | 241<br>(+288) | 247<br>(+307) | 126<br>(+186) | 102<br>(+151) | 108<br>(+155) | ND[a] |
| $T_g$ (°C) | 21 | −14 | −46 | −60 | −60 | −49 | −47 | −45 |

[a] Not determined.

a compromise between the extremes of high-power decoupling with high-truncation (artificial line-broadening) and low-power decoupling with low resolution (natural line-broadening). The $^{13}C$ chemical shift scale was externally referenced to tetramethylsilane (TMS) at 0.0 ppm using adamantane by setting the CH resonance to 38.5 ppm [59].

### 2.6. Solid-state NMR

Solid-state NMR spectroscopy of sample Copo3 was undertaken on a Bruker DRX500 spectrometer (Bruker BioSpin, Germany) operating at a $^{13}C$ Larmor frequency of 125.76 MHz using a 4 mm solid-state MAS NMR probehead and a MAS rotational frequency of 3.6 kHz. The copolymer Copo3 was packed into a 4 mm MAS rotor and the spectra recorded at a temperature of $-20\,^{\circ}C$ using 5120 transients. Semi-quantitative $^{13}C$ spectra were recorded using ramped-amplitude cross-polarization (ramp-CP) MAS [60], using a 4.0 μs 90° proton pulse, and a 500 μs contact time, TPPM dipolar decoupling (63 kHz) and a relaxation delay of 3 s. The contact time was optimized to give the highest intensity of the quaternary branch site at 48 ppm.

### 2.7. Melt-state NMR

Melt-state NMR spectra were recorded on various spectrometers using 7 mm MAS solid-state NMR probeheads. Samples were packed in zirconia rotors with boron nitride rotor caps and MAS rotational frequencies between 2.8 and 3.0 kHz were used. The sample temperature was calibrated for the given MAS conditions using lead nitrate and two other materials of known melting point [34,45]. For the homologous series of poly($n$-alkyl acrylates) a Bruker Avance-II-300 spectrometer (75.47 MHz), was used with a sample temperature of $T_g + 150\,^{\circ}C$ facilitating the need for a high temperature (>120 °C) MAS probehead for PMA and PEA. At lower temperatures resolution required for quantification was not achieved (see supporting information for PMA at $T_g + 100\,^{\circ}C$). For melt-state measurements of Copo1 and Copo3 a Bruker DSX300 spectrometer (75.47 MHz) was used whereas for Copo2EHA and Copo2 a Bruker DSX500 spectrometer (125.76 MHz) was used. For these two devices measurements were undertaken at 100 and 90 °C respectively. To insure quantitative spectra the $^{13}C$ $T_1$ relaxation times of poly($n$-butyl acrylate) were measured via the saturation recovery method at $T_g + 150\,^{\circ}C$, with $^{C}T_1$ for all sites found to range between 0.2 and 1.7 s. Quantitative $^{13}C$ spectra were recorded using single-pulse excitation, using a 5.0 μs 90° pulse, TPPM dipolar decoupling (42–50 kHz) and a relaxation delay of 10 s.

### 2.8. Quantification of the degree of branching from $^{13}C$ NMR

The degree of branching ($DB$) is defined as the percentage of branched to non-branched monomer units and may be quantified using the areas of the branched quaternary site $I(C_q)$ and of the non-branched tertiary carbon site $I(CH_t)$ [Fig. 2a,b, Eq. (1)].

$$DB(\%) = \frac{I(C_q)\cdot 100}{I(C_q) + I(CH_t)} \tag{1}$$

The $^{13}C$ chemical shifts for these systems have previously been reported as: 48, 41 39 and 35 ppm for the $C_q$, $CH_t$, $CH_s$ and $CH_2$ sites respectively [12,18,20,21]. Additionally the terminal methyl group of the 2-ethylhexyl acrylate monomeric unit (Fig. 2c) was observed at 11 ppm. [Full chemical shift assignment of 2-ethylhexyl acrylate and methyl acrylate monomeric units is given in the supporting information]. The same analysis method could be used for all homopolymer and copolymer systems as the chemical shift of the backbone sites used for quantification did not vary. All degrees of branching derived from solution-state spectra of poly($n$-alkyl acrylate) homopolymers were calculated using Eq. (1).

Inclusion of sites adjacent to the branch site into the denominator of Eq. (1) has also been demonstrated [12,18,19]. However, as these sites were not resolved in the solid-, swollen- and melt-state this approach was not used. Furthermore, for the swollen- and melt-state measurements of the homopolymers the backbone $CH_t$ and $CH_2$ signals were insufficiently resolved for reliable independent integration, and were thus integrated together and the degree of branching determined accordingly [Eq. (2)] [61]:

$$DB(\%) = \frac{I(C_q)\cdot 100}{I(C_q) + \frac{I(CH_t + CH_2)}{2}} \tag{2}$$

The integration ranges used were 50–48 and 45–33 ppm for $I(C_q)$ and $I(CH_t + CH_2)$ respectively. It should be noted that the backbone $CH_2$ group adjacent to the branch site is resolved with respect to the other backbone $CH_2$ sites, and as it is shifted toward the $CH_t$ sites it is included in $I(CH_t + CH_2)$ [14].

For poly(2-ethylhexyl acrylate), Heatley et al. [21] have previously shown that transfer to polymer occurs predominantly by abstraction of the hydrogen atom on the tertiary $CH_t$ from the backbone and not on the tertiary $CH_s$ from the side group (Fig. 2c). Therefore Eq. (2) holds. However, for all copolymers, as the $CH_t$ and $CH_s$ sites are not fully resolved the group integral $I(CH_t + CH_2 + CH_s)$ has to be corrected for the inclusion of $CH_s$. This was achieved through subtraction of $I(A)$, the resolved integral of methyl group A (Fig. 2c) (Eq. (3)).

$$DB(\%) = \frac{I(C_q)\cdot 100}{I(C_q) + \frac{I(CH_t + CH_2 + CH_s) - I(A)}{2}} \tag{3}$$

The integral ranges used were 50–48, 45–33 and 13–10 ppm for $I(C_q)$, $I(CH_t + CH_2 + CH_s)$ and $I(A)$ respectively.

### 2.9. Precision of NMR-determined degree of branching

To the authors knowledge limited attention has previously been paid to the issue of absolute error and precision of quantities derived from relative NMR integral calculations. Theoretically, for quantities derived from an $X = A/B$ type relationships where $B$ is large and $A$ tends to 0, the standard deviation (SD) of $X$ is inversely

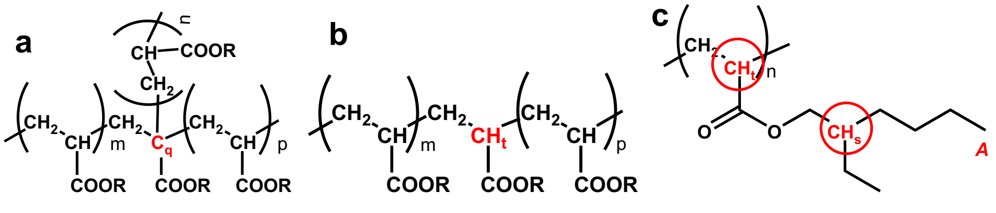

Fig. 2. Chemical structure of the (a) branched or (b) linear poly(alkyl acrylate) and (c) 2EHA monomer unit. The quaternary carbon $C_q$, tertiary carbons $CH_t$ and $CH_s$ and methyl group A are illustrated.

proportional to the signal-to-noise ratio (SNR) of A only (see later). Experimentally, however, the exponent to which the SNR is raised may deviate from its theoretical value of −1. For example, a value of −1.28 was experimentally demonstrated for polyolefin copolymers [Eq. (4)] [34,45].

$$\mathrm{SD}(\%) = \frac{238}{\mathrm{SNR}^{1.28}} \tag{4}$$

The value of −1.28 is, however, expected to be highly setup and material specific and thus cannot be applied as is [34]. To estimate SD, (Eq. (4)) necessitates the knowledge of only SNR of $C_q$, which can be estimated from a published spectrum. However, as it was established for polyethylene and melt-state NMR, it is questionable how transferable it is to measurements of other polymers by other NMR methods.

A similar approach was thus used involving the derivation of a rigorous expression for calculation of the SD of *DB* using the SNR of $C_q$ and the integral ranges used. Relative standard deviations for *DB* from Equations (1) to (3) are given in Equations (5) to (7) respectively:

$$\mathrm{SD}(\%) = \frac{100}{\mathrm{SNR}}\cdot\sqrt{\frac{\Delta f_q^2\cdot I(\mathrm{CH_t})^2+\Delta f_t^2\cdot I(\mathrm{C_q})^2}{\Delta f_q^2\cdot\left(I(\mathrm{C_q})+I(\mathrm{CH_t})\right)^2}} \tag{5}$$

$$\mathrm{SD}(\%) = \frac{100}{\mathrm{SNR}}\cdot\sqrt{\frac{\Delta f_q^2\cdot I(\mathrm{CH_t}+\mathrm{CH_2})^2+\Delta f_t^2\cdot I(\mathrm{C_q})^2}{\Delta f_q^2\cdot\left(2\cdot I(\mathrm{C_q})+I(\mathrm{CH_t}+\mathrm{CH_2})\right)^2}} \tag{6}$$

$$\mathrm{SD}(\%) = \frac{100}{\mathrm{SNR}}\cdot\sqrt{\frac{\Delta f_q^2\cdot\left(I(\mathrm{CH_t}+\mathrm{CH_2}+\mathrm{CH_s})-I(\mathrm{A})\right)^2+\left(\Delta f_t^2+\Delta f_A^2\right)\cdot I(\mathrm{C_q})^2}{\Delta f_q^2\cdot\left(2\cdot I(\mathrm{C_q})+I(\mathrm{CH_t}+\mathrm{CH_2}+\mathrm{CH_s})-I(\mathrm{A})\right)^2}} \tag{7}$$

where $\Delta f_q$, $\Delta f_t$ and $\Delta f_A$ are the widths of the spectral integration range for $I(\mathrm{CH_q})$, $I(\mathrm{CH_t}+\mathrm{CH_2}+\mathrm{CH_s})$ (or $I(\mathrm{CH_t}+\mathrm{CH_2})$ or $I(\mathrm{CH_t})$) and $I(\mathrm{A})$, respectively. The derivations will be detailed in a future manuscript. Unfortunately this approach has limited applicability to previously published spectra due to the need of knowing the integral ranges used as well as the SNR.

The SNR was calculated using the Bruker command of “sino real” to limit deviations due to baseline correction applied to only the real part of the spectrum, and 10 ppm wide noise region was used. For published spectra, SNR was estimated as 2.5 times the ratio of the $C_q$ peak intensity to the peak-to-peak noise of the baseline [62]; it was assumed that the shown spectrum is representative, and that all branching levels determined in the same publication have the same relative precision.

## 3. Results and discussion

### 3.1. Branch quantification by solution-state NMR

Due to the spare occurrence of branching, low sample concentrations and inherent low sensitivity of $^{13}$C NMR, low signal-to-noise ratios for the $C_q$ site were expected for all solution-state measurement. The sensitivity of the different NMR methods was compared through the use of the SNR of the $C_q$ site.

The poly(*n*-alkyl acrylate) homopolymers exhibited high resolution (Fig. 3) and SNR values of $C_q$ sufficient for branch quantification (Table 3), albeit with limited precision. No significant difference

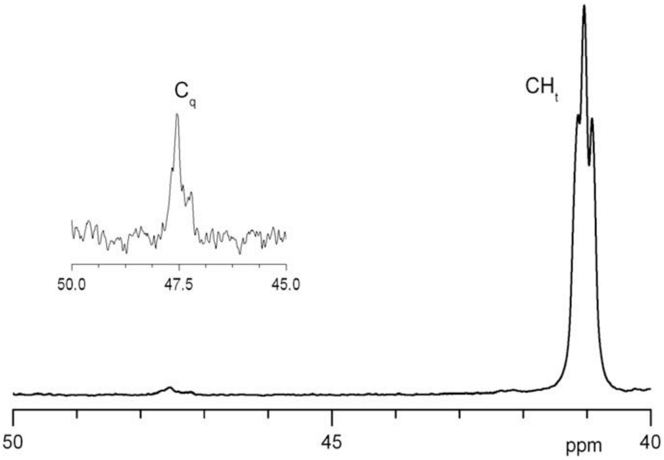

**Fig. 3.** Partial solution-state $^{13}$C NMR spectrum of PMA showing the $C_q$ and $CH_t$ signals used for quantification at 47.5 and 41 ppm respectively (spectrum recorded in 54 h).

could be detected between the homopolymers with all systems exhibiting a degree of branching of around 2% by solution-state NMR. In contrast branching could not be detected for the copolymers, even with longer measurements at elevated temperatures (see supporting information). This may have been a result of the high gel fraction preventing a significant proportion of the sample from going into solution. Alternative NMR methods were thus sought for branch quantification of these materials, including bulk-state NMR as this had previously been demonstrated to be highly sensitive to low degrees of branching in polyethylene [34]. Bulk polymer analysis also removed the risk of not measuring the microgels present, and is thus deemed the preferred choice for such systems.

### 3.2. Branch quantification by swollen-state NMR

The comparison of swollen-, solid- and melt-state NMR was undertaken on Copo3 as this material was likely to exhibit the highest degree of branching due to the high polymerization temperature [2]. The swelling agent for swollen-state was chosen to be a good solvent of alkyl acrylate monomeric units as well as having a relatively high boiling point to avoid evaporation during measurement. Due to their relative polarity, poly(alkyl acrylates) with short side groups are soluble in polar solvents, aromatic hydrocarbons and chlorinated hydrocarbons; common solvents include THF, dimethylformamide (DMF), acetone, butanone, ethylacetate and chloroform [63]. In contrast, the swelling ability of the solvents increases in the following order: alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, ketones and esters [7]. Thus DMF and THF are good swelling agents for the poly(alkyl acrylates). Although DMF had a high boiling point solvent peaks obscured the backbone sites in the $^{13}$C NMR spectra (supporting information). The $^{13}$C NMR spectrum obtained for Copo3 swollen with 50% THF exhibited a resolution acceptable for branch detection (Fig. 4a). However, with a SNR of only 2.8 achieved in 4.5 h accurate branch quantification was not deemed possible. An acceptable precision of 20% would only be achieved with 28 h of measurement (SNR scaling with the square root of measuring time [62]).

**Table 3**
Branch quantification results for the various NMR methods used showing the degree of branching (*DB*), absolute standard deviation of *DB* (Eq. (4)), SNR of $C_q$ and the measurement time.

| Sample | Solution-state | Swollen-state MAS | Solid, CP-MAS | Melt-state MAS |
|---|---|---|---|---|
| PMA | 2.1 ± 0.3 (9 in 54 h) | ND[a] | ND[a] | 1.92 ± 0.06 (30 in 43 h) |
| PEA | 1.6 ± 0.4 (6 in 58 h) | ND[a] | ND[a] | 1.31 ± 0.07 (19 in 45 h) |
| PnBA | 2.3 ± 0.9 (4 in 54 h) | ND[a] | ND[a] | 2.21 ± 0.09 (25 in 49 h) |
| PHxA | 1.8 ± 0.8 (3.5 in 54 h) | ND[a] | ND[a] | 2.26 ± 0.16 (16 in 45 h) |
| Copo1 | Impossible | ND[a] | ND[a] | 5.16 ± 0.41 (14 in 14 h) |
| Copo2 | Impossible | ND[a] | ND[a] | 3.43 ± 0.14 (24 in 18 h)[b] |
| Copo3 | Impossible | 5.37 ± 3.44 (2.8 in 4.5 h) | low resolution (5.1 in 4.5 h) | 6.10 ± 0.27 (23 in 28 h, i.e. 8 in 3.5 h |
| Copo2EHA | Impossible | ND[a] | ND[a] | 4.75 ± 0.17 (26 in 18 h)[b] |

[a] Not determined.

[b] Measurement carried out at a higher Larmor frequency (125 vs 75 MHz) in an attempt to speed up quantification; this slightly increased the SNR but also introduced spinning side bands between 0 and 60 ppm, which could interfere with the branching quantification.

### 3.3. *Branch quantification by solid-state NMR*

An alternative possible approach for achieving high SNR of the branch site is through solid-state using CP-MAS at sub-ambient temperatures. No previous reports of this approach for polyacrylates have been found in the literature. As expected the CP-MAS solid-state NMR spectrum showed limited resolution (Fig. 4b) and deconvolution was necessary in order to quantify the degree of branching. The use of deconvolution on such broad lines is expected to lower the overall precision of the determined degree of branching. When compared to the swollen-state NMR spectra an increase in SNR was observed from 2.8 to 5.1 (Table 3). Such a small increase in SNR only results in a limited improvement of the accuracy however (Eq. (4)).

Due to the different polarization transfer dynamics related to rigidity and number of proximal protons CP-MAS spectra are generally only approximately quantitative. The local nanophase separation observed in poly(alkyl acrylates) above $T_g$ [55] may also influence the CP dynamics of PnBA, PHxA, and the copolymers at $-20$ °C. Note that if needed, correction factors could be determined via comparison to quantitative single-pulse excitation experiments. In general, however, the low resolution of the solid-state NMR spectra results in this technique not meriting further investigation for branch quantification.

### 3.4. *Branch quantification by melt-state NMR*

In the molten state branch quantification also includes any insoluble fractions, be they crosslinked or high molar mass. To assess the risk of decomposition in the melt thermogravimetric analysis was undertaken, this insured degradation was unlikely at measurement temperatures of $T_g + 150$ °C. The melt-state NMR spectrum obtained for Copo3 showed resolution intermediate to that obtained by swollen- and solid-state NMR (Fig. 4c), and was only moderately less than that achieved in the swollen-state. Furthermore, due to this being a bulk-state measurement high-sensitivity is achieved. The SNR of 8 obtained in 3.5 h was also showed the highest obtained in the least time out of all NMR methods (Table 3), again illustrating the melt-state NMR methods suitability for branch quantification.

With the melt-state method having been shown to be the most sensitive all poly(alkyl acrylates) were measured and the branching quantified (Table 3). The high-SNR melt-state NMR spectrum of Copo3 is shown in Fig. 5 and the reader is directed to the supporting information for other high-SNR quantitative spectra.

### 3.5. *Observed degrees of branching and their precision*

As for all experimentally determined quantities, the precision of the degree of branching is also of high importance. As well as the basic method for the calculation of the absolute SD of *DB* (Eq. (4)) a more rigorous method (Eqs. (5) to (7)) was also applied. Limited differences were seen between these two approaches, however, and all trends remained the same (Table 4). Larger differences between the two methods were seen for solution-state measurements, but this may be due to the limited applicability of (Eq. (4)), established for melt-state polyethylene spectra, to solution-state data. With the SD values obtained using the basic method being larger and the ability to retroactively apply the method to pre-published spectra, only these values will be further discussed.

As expected the degree of branching was significantly higher for the copolymers polymerized in emulsion under monomer-starved conditions than for the homopolymers polymerized in solution. The quantitative results for the homologous series of poly(*n*-alkyl acrylate) homopolymers showed that PEA had a significantly lower degree of branching than the other members. Importantly this difference was not observed through solution-state NMR measurements alone, due to insufficient sensitivity. Through comparison of Copo2EHA and Copo1 it was shown that the introduction of methyl acrylate comonomer did not significantly affect the degree of branching in the poly(2-ethylhexyl acrylate) homopolymer. The degree of branching was shown to increase with synthesis temperature for radical polymerization in emulsion under monomer-starved conditions by comparing Copo2 and Copo3, which is consistent with the branching resulting mostly from intramolecular transfer to polymer [2].

The group of Lovell [18,21] measured degrees of branching in 2-ethylhexyl acrylate and *n*-alkyl acrylate homopolymers in the solution-state and observed significantly more branching in poly(2-ethylhexyl acrylate) and significantly less branching in poly(ethyl acrylate). With the same observation confirmed here it may be concluded that the lateral ester group plays a role in polyacrylates branch formation under radical solution polymerization. The observation of Plessis et al. concerning the influence of initiator concentration [12,20], feeding time [12], and styrene comonomer concentration [14] on the degree of branching may be considered significant with SNR of 16, 6 and 5 and SD of 7, 25 and 30% respectively for Refs [12,14,20]. However, when the coefficient of intramolecular transfer to polymer was determined the initial results had a limited precision with SNR of 5.5 and SD of 25% leading to a 50% standard deviation for the kinetic coefficient [2]. This 50% standard deviation makes the kinetic coefficients consistent with new values of coefficient of intramolecular transfer to polymer, which were recently determined by Nikitin et al. using a novel (indirect) technique based on pulsed-laser polymerization [25]. Further comparison of the two techniques requires more accurate NMR measurements preferably based on the melt-state NMR technique, which has shown great potential in the case of polyacrylates for the determination of such accurate kinetics coefficients.

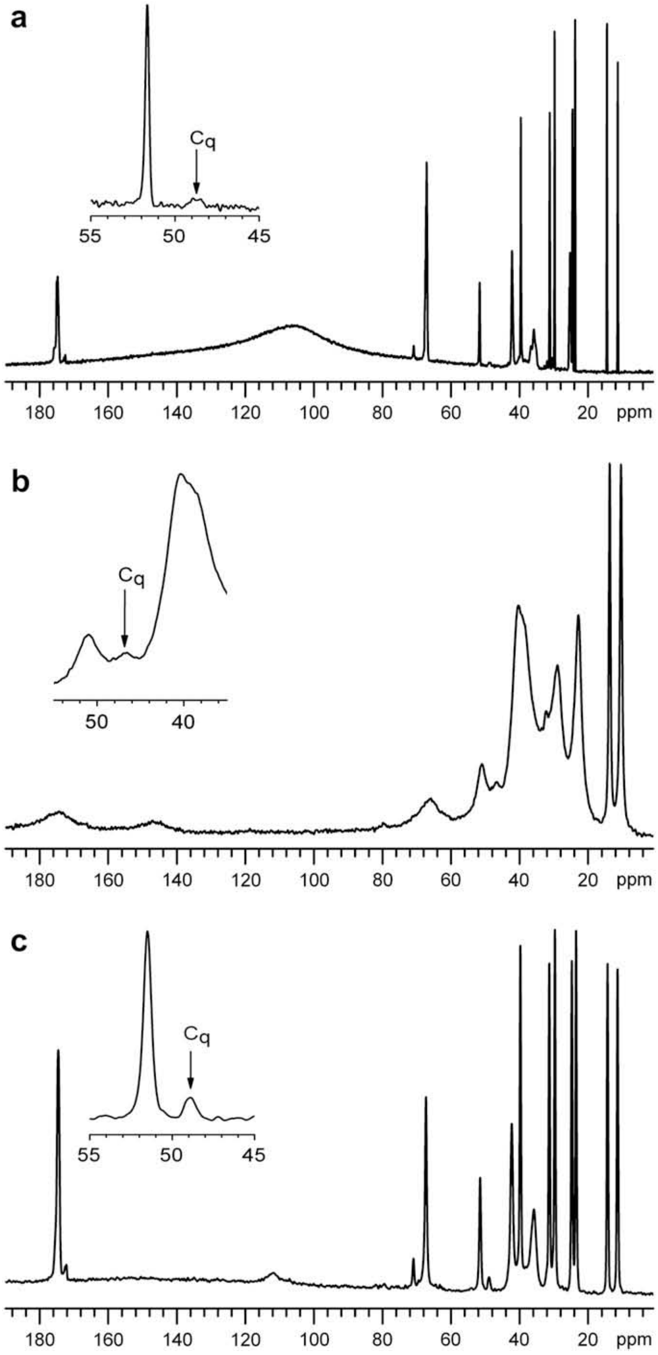

**Fig. 4.** $^{13}$C spectra of Copo3 measured by (a) SPE-MAS swollen-state, (b) CP-MAS solid-state and (c) SPE-MAS melt-state NMR, illustrating the resolution and sensitivity (spectra recorded in 3.5–4.5 h). The broad line centered on 105 ppm in the swollen-state spectrum arises from the KelF MAS rotor cap.

Examples are present in the literature with limited SNR of ca 3 and thus high SD of ca 70% in the degree of branching, however, such variation might not be significant during emulsion polymerization in the presence of cross-linker [64,65].

### 3.6. Conventional detection and quantification of long-chain branching by multiple-detection SEC

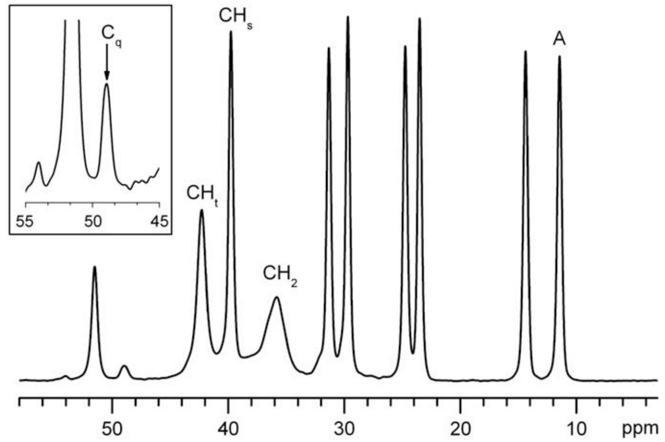

**Fig. 5.** $^{13}$C spectrum of Copo3 recorded in 28 h with SPE-MAS melt-state NMR, illustrating the resolution and high-sensitivity, and showing the signals used for quantification.

NMR can yield accurate values of degree of branching, but cannot discriminate between short- and long-chain branching. The two types of branching have however different influence on rheological properties, solution properties, etc. and many efforts have been devoted to detection and quantification of long-chain branching using rheology or chromatography.

The presence of long-chain branching may be confirmed by comparison of the radius of gyration or intrinsic viscosity to a linear system at the same hydrodynamic volume [1]. The latter method has previously been used to determine the degree of LCB [66,67] through the use of the ratios $g' = [\eta]_B/[\eta]_L$ and $g = R_{g,B}/R_{g,L}$, where $[\eta]_B$ and $[\eta]_L$ are the intrinsic viscosities and $R_{g,B}$ and $R_{g,L}$ are the radii of gyration of the branched and the linear chains respectively. The strong limitations of this method to quantify LCB have previously been discussed in Refs. [1,68]. One such limitation is that the dispersity at each elution time $t_{el}$ (local dispersity) should be small [6,69], which is not the case for the PMA (Fig. 7a) and PEA systems studied here [3]. The recently proposed approach of comparing molecular weight distributions calculated from rheology and measured by SEC is also promising to quantify LCB [70]. However, due to incomplete separation, the determination of the true molecular weight distribution of the sparsely branched polyacrylates in this work is not possible.

Although it is not currently possible to quantify long-chain branching in polyacrylates, its detection is possible. In this part, we are using the conventional comparison of samples with linear

**Table 4**
The quantified degrees of branching (*DB*), the signal-to-noise ratio (SNR) of the branch site C$_q$ and the absolute standard deviations (SD) of *DB* calculated using the basic (Eq. (4)) and rigorous (Eqs. (5)–(7)) methods and their relative difference.

| NMR method | Sample | *DB* (%) | SNR | SD[a] from (Eq. (4)) | SD[a] from (Eqs. (5) to (7)) | Diff. SD[b] |
|---|---|---|---|---|---|---|
| Melt-state | PMA | 1.92 | 30 | 0.058 | 0.062 | −7.2% |
| | PEA | 1.31 | 19 | 0.072 | 0.068 | 5.4% |
| | PnBA | 2.21 | 25 | 0.087 | 0.088 | −1.0% |
| | PHxA | 2.26 | 16 | 0.160 | 0.142 | 12% |
| | Copo1 | 5.16 | 14 | 0.408 | 0.346 | 16% |
| | Copo2 | 3.43 | 24 | 0.137 | 0.140 | −1.9% |
| | Copo3 | 6.10 | 23 | 0.268 | 0.280 | −4.6% |
| | Copo2EHA | 4.75 | 26 | 0.172 | 0.182 | −5.6% |
| Solution-state | PMA | 2.1 | 9 | 0.307 | 0.233 | 27% |
| | PEA | 1.6 | 6 | 0.379 | 0.259 | 38% |
| | PnBA | 2.3 | 4 | 0.874 | 0.536 | 48% |
| | PHxA | 1.8 | 3.5 | 0.794 | 0.473 | 51% |

[a] The absolute SD is the relative SD obtained from (Eqs. (5) to (7)) multiplied by DB.
[b] Diff SD was calculated as the hundredfold of the difference between the absolute SD values shown in columns 5 and 6, divided by their arithmetic mean.

equivalents. Since no branching or reactions potentially leading to branching have been reported for anionic polymerizations of acrylates [71], poly(alkyl acrylates) obtained by this method are likely to be linear. For the poly(*n*-alkyl acrylates) materials studied here only the solution properties of a linear PnBA equivalent are known in the literature. The intrinsic viscosity of a linear PnBA was thus calculated from the conventional calibration curve of polystyrene and the Mark–Houwink–Sakurada (MHS) parameters of the polystyrene and linear PnBA (Table 5). The calculated intrinsic viscosity showed good agreement when overlayed with the measured data of PnBA (Fig. 6) and showed the absence of LCB in PnBA.

The occurrence of LCB, and high degrees of SCB, may also be deduced via comparison of the MHS parameters with those of linear chains [78]. A comparison of MHS parameters for the polyacrylates studied here and those previously published is thus possible (Table 5). For poly(*n*-butyl acrylate) comparable MHS parameters were obtained for systems polymerized by anionic and radical polymerization, again confirming the absence of LCB after conventional radical polymerization. It should be noted, that controlled (nitroxide-mediated) polymerization of *n*-butyl acrylate has been shown to not produce LCB [19], except when targeting high molecular weights at high conversion [3]. For poly(2-ethylhexyl acrylate) two publications yielded the same MHS parameters for different samples obtained by anionic polymerization and characterized either via off-line viscometry/light scattering (LS) or via SEC with online viscometer and universal calibration (UC). This confirmed the absence of LCB after anionic polymerization of acrylates as well as the accuracy of the determination of intrinsic viscosity and molecular weight off-line or after SEC. In the case of radical polymerization of 2-ethylhexyl acrylate, the MHS parameters of samples are significantly different from those of linear systems, whatever the conditions used for the radical polymerization. Note that one set of MHS parameters has been determined for samples polymerized at low temperature (12 °C), expecting no LCB. This reasonable assumption was proved incorrect as P2EHA obtained by conventional radical polymerization was shown to be branched, even when polymerized at low temperature. The same observations hold for PtBA with conventional radical polymerization of *t*-butyl acrylate leading to LCB in the polymer chains. Additional discussion on the MHS parameters of polyacrylates is given at the end of the supporting information.

**Table 5**
Determined and previously published Mark–Houwink–Sakurada parameters ($K$ and $\alpha$) for poly(*n*-butyl acrylate), poly(2-ethylhexyl acrylate) and poly(*t*-butyl acrylate) systems.

| Polymer | $K \cdot 10^5$ (dL g$^{-1}$) | $\alpha$ | Polymerization | Determination of $K$ and $\alpha$ | Refs. |
|---|---|---|---|---|---|
| PnBA | 12.2 | 0.700 | Radical | TD SEC at 30 °C | [72] |
| | 11.8 | 0.716 | Anionic | SEC UC at 25 °C | [73] |
| P2EHA | 130 | 0.39 | Radical 70 °C | TD SEC at 30 °C | This work |
| | 11.1 | 0.68 | Radical 50–70 °C | Viscometry – light scattering at 25 °C | [58] |
| | 8.2 | 0.695 | Radical | TD SEC at 30 °C | [72] |
| | 12.4 | 0.67 | Radical 12 °C | Viscometry – light scattering at 25 °C | [74] |
| | 2.5 | 0.803 | Anionic | SEC UC at 25 °C | [73] |
| | 2.6 | 0.815 | Anionic | Viscometry – light scattering at 25 °C | [75] |
| PtBA | 3.33 | 0.8 | Anionic | Viscometry + MALLS | [76] |
| | 3.33 | 0.8 | Anionic | SEC UC at 25 °C | [77] |
| | 43.4 | 0.6 | Radical 70 °C | Viscometry – light scattering at 25 °C | [58] |
| | 2.6 | 0.79 | PLP 50 Hz, 20 °C | TD SEC at 30 °C | This work |
| | 10 | 0.77 | PLP 100 Hz, 20 °C | TD SEC at 30 °C | This work |

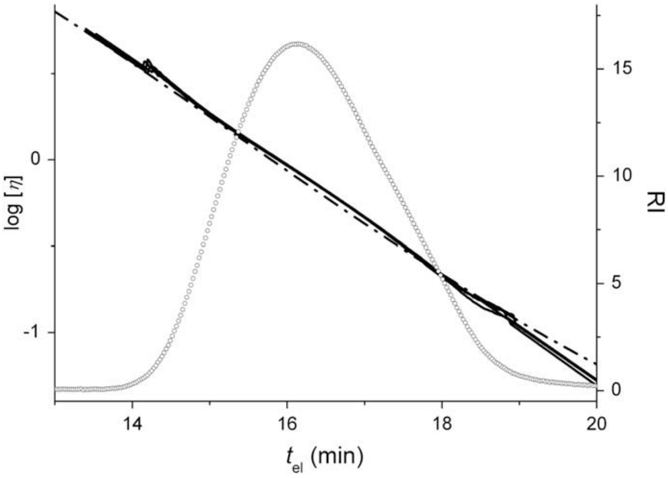

**Fig. 6.** Intrinsic viscosities (log [$\eta$]) against elution time ($t_{el}$) of PnBA obtained by universal calibration using Mark–Houwink–Sakurada parameters (dashed dotted line) and online viscometer (solid black line). The SEC chromatogram given by the refractive index detector (RI) is shown as a function of $t_{el}$ (hollow circles).

Comparison of the intrinsic viscosity or Mark–Houwink–Sakurada parameters of the samples with linear equivalents allows to detect long-chain branching in P2EHA and PtBA and show its absence in PnBA. The technique is however limited since no data are available on linear PMA, PEA and PHA for example. Linear equivalent would also prove difficult to obtain, if possible at all, e.g. in the case of starch. Another limitation of the technique is the sensitivity: melt rheological measurements are more sensitive to LCB than SEC using comparison with linear equivalent [79–81].

### 3.7. A novel method for detection of long-chain branching by multiple-detection SEC

We are investigating whether SEC could allow detection of long-chain branching, even without using a linear equivalent. The validity of the universal calibration principle for poly(alkyl acrylates) with the organic columns used in this work and THF as eluent has previously been demonstrated in Ref. [3]. However, for some polyacrylates the molecular weights determined by UC using online viscometer may be different from those determined by light-scattering based methods. This was indeed the case for PEA studied here with UC/viscometer yielding lower molecular weights than LS (Fig. 5a of Ref. [3]). The importance of data treatment [82] and the related misnomer "anomalous elution" have been already discussed and taken into account [3]. The difference in molecular weights determined by UC and LS is explained by an incomplete separation in terms of molecular weights by SEC due to the separation being based upon hydrodynamic volume, with chains of the same hydrodynamic volume having different molecular weights due to the presence of LCB [3,49,50]. Incomplete separation has been recently confirmed to occur for model linear and branched polystyrenes by two-dimensional chromatography (molecular-topology fractionation × SEC) [83]. Instead of the presence of LCB, the effect could be due to shear-degradation of largest molecules, especially if they exhibit high levels of branching. Shear-degradation has been shown to happen in the case of ultra-high molecular weight polymers [84]. Shear-degradation is very unlikely in this work since molecular weights are too limited and the incomplete separation is also observed in the case of even lower molecular weights polyacrylates obtained by nitroxide-mediated polymerization [3]. Incomplete separation due to shear-degradation may however take place in the case of other higher molecular weight branched polymers, especially polyethylene and starch.

Incomplete SEC separation was observed for PMA and was most prominent in the elution time range corresponding to the maximum signal of the refractive index detector (RI, Fig. 7a). For PnBA and PHxA no significant difference between molecular weights determined by universal calibration/viscometry and light scattering were observed (Fig. 7b and c), especially around the maximum RI signal. This result is consistent with the comparison of intrinsic viscosity of this polymer with linear one (see 3.5). This implies that all the branching quantified in PnBA by NMR spectroscopy was short-chain branching.

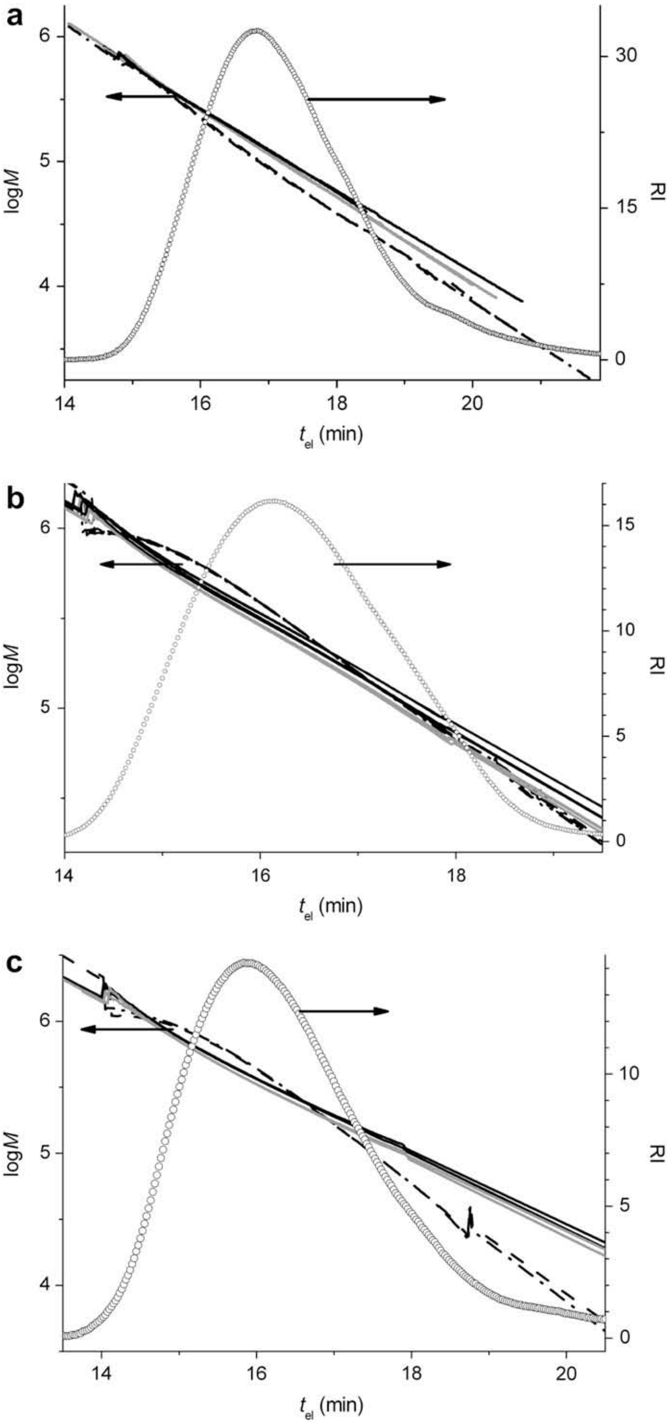

**Fig. 7.** Molecular weights (log *M*) obtained through universal calibration (dashed dotted line), triple detection (solid gray line) and low-angle laser light scattering (solid black line) against elution time ($t_{el}$) for (a) PMA, (b) PnBA and (c) PHxA. SEC chromatogram given by the refractive index detector (RI) are also shown (hollow circles) as a function of $t_{el}$.

In contrast, for PHxA differences in molecular weights were observed in the high elution volume range, however this may have been an artifact due to data treatment [3,82] and cannot be purely attributed to the presence of LCB. No conclusion can be drawn on the presence of LCB or not in PHxA.

With the quality of the SEC separation able to be assessed through the use of multiple-detection, it may also be used as a means of detecting LCB. The comparison of molecular weights determined by UC and LS has been shown to be very sensitive to low degrees of LCB, due to the dramatic changes of hydrodynamic properties of polymers with the presence of only a few long branches [3,68]. In contrast, short branches (SCB) only have limited effect on hydrodynamic volume and thus on SEC separation; therefore they will not be detected. With even sparse amounts of LCB able to significantly change mechanical properties, sensitive methods of LCB detection are clearly needed [38]. For the homologous poly(*n*-alkyl acrylate) series studied here LCB was detected for PMA and PEA but not for PnBA. When comparing molecular weights determined by UC and LS, one has to be aware of artifacts in the molecular weight determined in the elution region where the refractometer trace is weak (low elution time) or when the light-scattering trace is weak (high elution time) [3]. Thus, the noise in multiple-detection SEC signals is the main limitation of LCB detection by this method [82].

## 4. Conclusion

Through the combination of $^{13}$C NMR and multiple-detection SEC insight into the branching process in polyacrylates was achieved. Results obtained by both methods were found to be comparable to or more accurate than those previously published.

The high-sensitivity of melt-state NMR allowed meaningful quantification of branching in polyacrylates for the first time by overcoming both the solubility and sensitivity issues commonly encountered. Degrees of branching of the order of 2% of the monomer units with a relative precision of 10–25% in 5 h, or 4–7% within 45 h, were able to be determined. Through this significant gain in precision accurate determination of kinetic coefficients for the intramolecular transfer to polymer [2] should hopefully be facilitated. This reaction is the key to fully understand and describe the kinetics of radical polymerization of acrylates: this will allow a better control of the industrial production processes, as well as of the obtained material properties. Further significant improvements in sensitivity are also expected through optimization of the melt-state method specifically for polyacrylates, as was achieved for polyolefins [34].

Irrespective of the polymerization process the degree of SCB for poly(methyl acrylate), poly(*n*-butyl acrylate) and poly(*n*-hexyl acrylate) were found to be comparable, with lower and higher degrees observed for poly(ethyl acrylate) and poly(2-ethylhexyl acrylate) respectively. It is thus concluded that the nature of the lateral ester group is likely to influence the rate of intramolecular transfer to polymer in radical polymerization of acrylates, i.e. as the size of the alkyl side group increases the rate first decreases and then increases. Establishing such a relation between the size of the alkyl side group and the propagation rate coefficient ($k_p$) may not be possible. Although LCB may not play a significant role in actual kinetics of some of the systems studied, its presence does complicate the study of the kinetics process itself by pulsed-laser polymerization (PLP), the IUPAC-recommended technique for determining $k_p$. Due to the introduction of significant error in the determined molecular weight distribution, the values of $k_p$ determined by PLP for poly(methyl acrylate) [85], poly(ethyl acrylate) [56], poly(*t*-butyl acrylate) [56] and poly(2-ethylhexyl acrylate) [56,72] do not have the usual high accuracy usually seen for PLP-SEC experiments. The occurence of incomplete separation is especially important in the low-molecular weight region of the MWD and this is the part used (inflection point) in PLP experiments. Thus it may be required to reconsider the possible variation of the propagation rate coefficient with the size of the alkyl side group [22]. Multiple-detection SEC was shown to allow the detection of very sparse LCB, based upon incomplete SEC separation. This method uses what is a limit of common approaches of LCB detection such as the Zimm–Stockmayer method [67,86] where limited dispersity at each elution volume (i.e. complete separation in terms of molecular weight) is assumed. Combined with the known limitations of the method [1,68] it is concluded that the Zimm–Stockmayer method does not allow accurate indications of LCB in complex polyacrylates. The proposed multiple-detection SEC approach could be also applied to detect LCB in polyethylene [80] or amylose [87].

In general further insight into separation according to LCB as well as the quantification of LCB is needed. Several new separation methods such as gradient interaction chromatography [88], liquid chromatography at the critical condition [89], temperature gradient interaction chromatography [90], topology fractionation method [83] offer interesting possibilities for the future. Alternatively, the approach of Fourier-transform rheology could also be used to investigate LCB in polyacrylates [37]. This approach has also recently been combined with melt-state NMR to provide insight into the branching topology of polyethylenes [38]. A comparison of our multiple-detection SEC method to melt rheological measurements has still to be undertaken but these two methods should be complementary.

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## Appendix. Supplementary material

Supplementary material can be found, in the online version, at 10.1016/j.polymer.2009.03.021.

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