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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.

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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 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 chaing 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 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 *et al*. [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 reolution 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 quantative 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 above its glass transition temperature T_g, wether 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 respectivly. 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 [56].

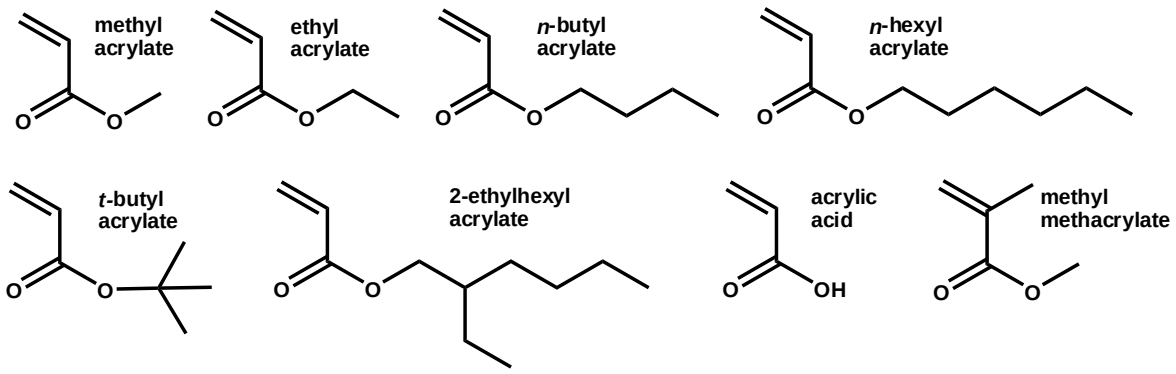

Fig. 1: Chemical structures of the acrylic monomers of the investigated polymers.

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 poly(alkyl acrylates) produced in this mannor 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 been described [3].

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 %)

2.2. 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-transistion temperatures previously determined by differential scanning calorimatory (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.

Table 2.

Decomposition temperatures (*DT*) and glass-transsition 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 (+206)	234 (+248)	241 (+288)	247 (+307)	126 (+186)	102 (+151)	108 (+155)	ND[a]
T_g (°C)	21	-14	-46	-60	-60	-49	-47	-45

[a] not determined

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 [3]. Injections were performed at 6-7 $g \cdot L^{-1}$, 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 $mL \cdot g^{-1}$ 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.

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 $g \cdot L^{-1}$ in $CDCl_3$ were used and spectra recorded at temperatures between at 29-33 °C using 19 500 to 21 000 transients. For the copolymer Copo2EHA a polymer solution of < 20 $g \cdot L^{-1}$ 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 19808 and 20267 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 centeral 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 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 - 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 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 °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 of 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 °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°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 °C, with $^{C}T_1$ for all sites found to range between 0.2 - 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)].

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

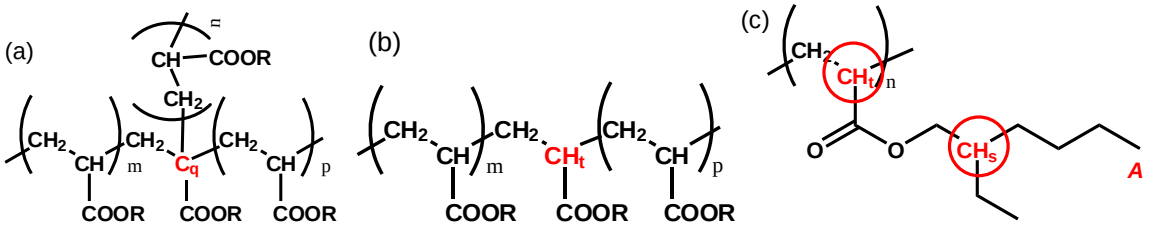

Fig. 2: Chemical structure of the (a) branched or (b) linear poly(alkyl acrylate) and (c) 2EHA monomer unit. The quaternary carbon C_q, tertiary carbons CH_t and CH_s and methyl group A are illustrated.

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]:

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

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 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)).

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

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 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].

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

The value of -1.28 is, however, expected to be highly setup-up and material specific and thus can not 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:

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

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

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

where Δf_q, Δf_t and Δf_A are the widths of the spectral integration range for $I(CH_q)$, $I(CH_t+CH_2+CH_s)$ (or $I(CH_t+CH_2)$ or $I(CH_t)$) and $I(A)$, 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 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 deamed the preferred choice for such systems.

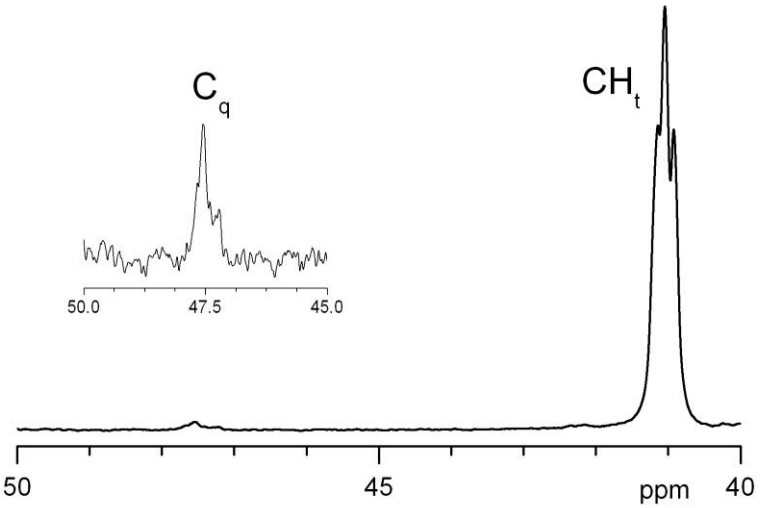

Fig. 3: Partial solution-state ^{13}C NMR spectrum of PMA showing the C_q and CH_t signals used for quantification at 47.5 and 41 ppm respectively (spectrum recorded in 54 h).

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 h 30)	low resolution (5.1 in 4 h 30)	6.10 ± 0.27 (23 in 28 h, i.e. 8 in 3 h 30)
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.

3.2. Branch quantification by swollen-state NMR

The comparion of swollen-state, solid-state 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 relativly 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 aceptable for branch detection (Fig. 4a). However, with a *SNR* of only 2.8 achieved in 4.5 h accurate branch quantification was not deamed 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]).

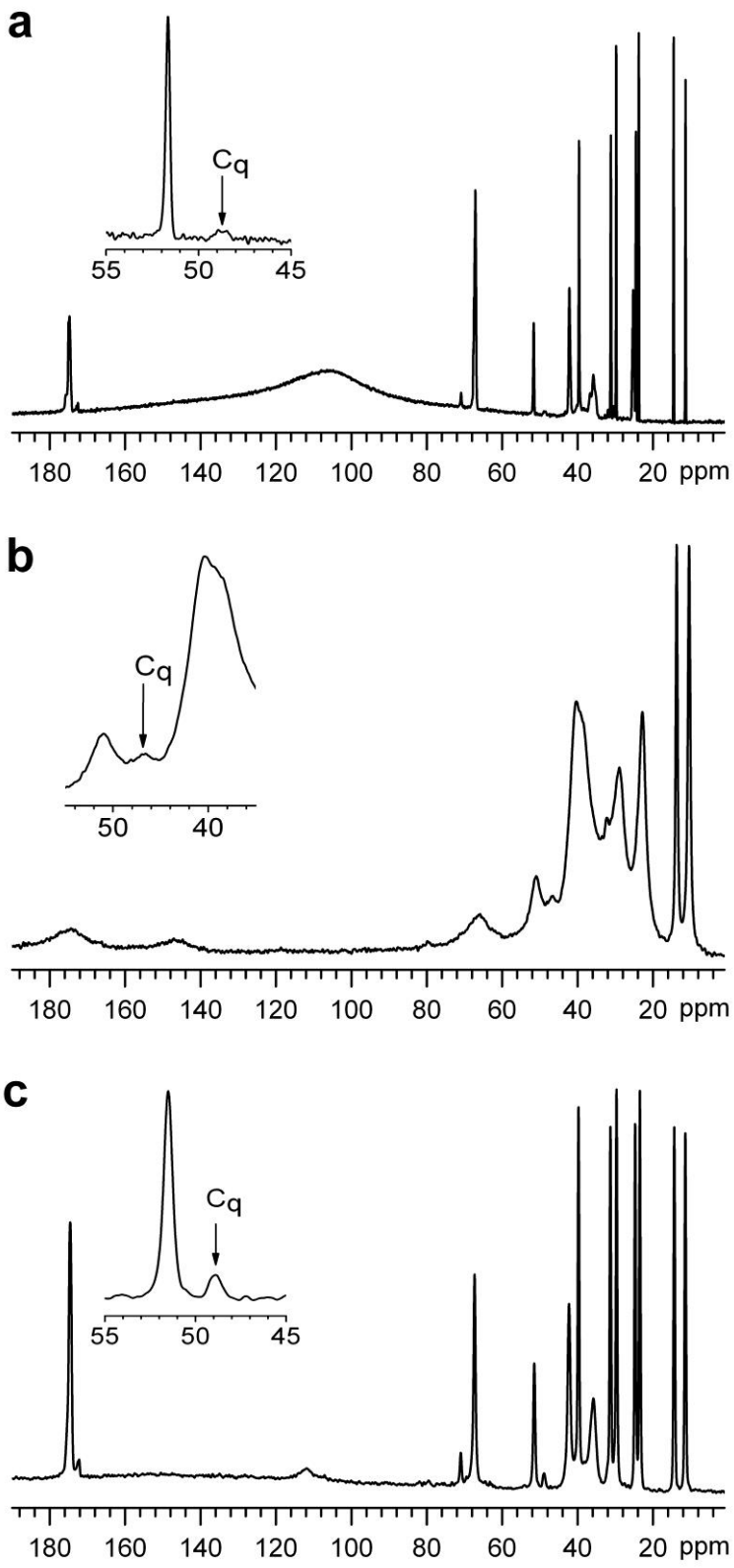

Fig. 4. ^{13}C spectra of Copo3 measured by (a) SPE-MAS swollen-state, (b) CP-MAS solid-state and (c) SPE-MAS melt-state NMR, illustrating the resolution and sensitivity (spectra recorded in 3.5 to 4.5 h). The broad line centered on 105 ppm in the swollen-state spectrum arises from the KelF MAS rotor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

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 on Fig. 5 and the reader is directed to the supporting information for other high-*SNR* quantitative spectra.

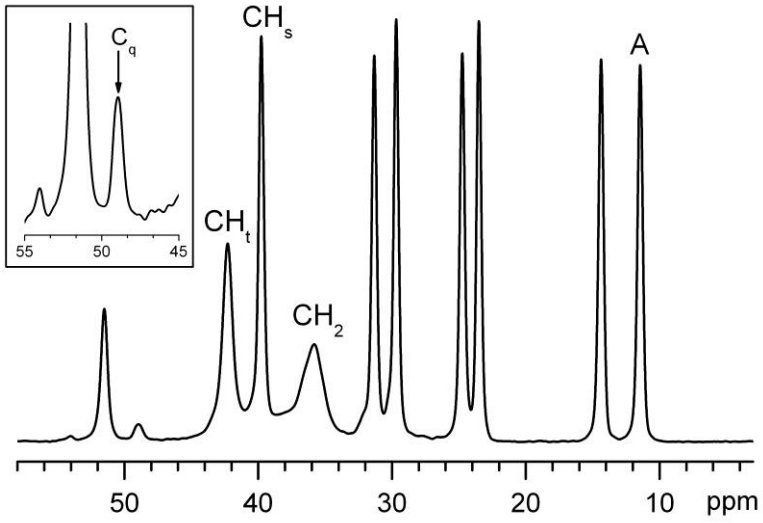

Fig. 5: ^{13}C spectrum of Copo 3 recorded in 28 h with SPE-MAS melt-state NMR, illustrating the resolution and high-sensitivity, and showing the signals used for quantification.

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 (Eq. (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.

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 (Eq. (5) to (7)) methods and their relative difference.

NMR method	Sample	*DB*, %	*SNR*	*SD*[a] from Eq. (4)	*SD*[a] from Eq. (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 Eq. (4) 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

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].

Lovell *et al*.[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 references [12], [14] and [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.

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

NMR can yield accurate values of degree of branching, but can not 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 [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 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 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.

Table 5.

Determined and previously published Mark-Houwink-Sakurada parameters (K and α) for poly(*n*-butyl acrylate), poly(2-ethylhexyl acrylate) and poly(*t*-butyl acrylate) systems.

Polymer	$K \cdot 10^5$ ($dL \cdot g^{-1}$)	α	Polymerization	Determination of K and α	Ref.
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

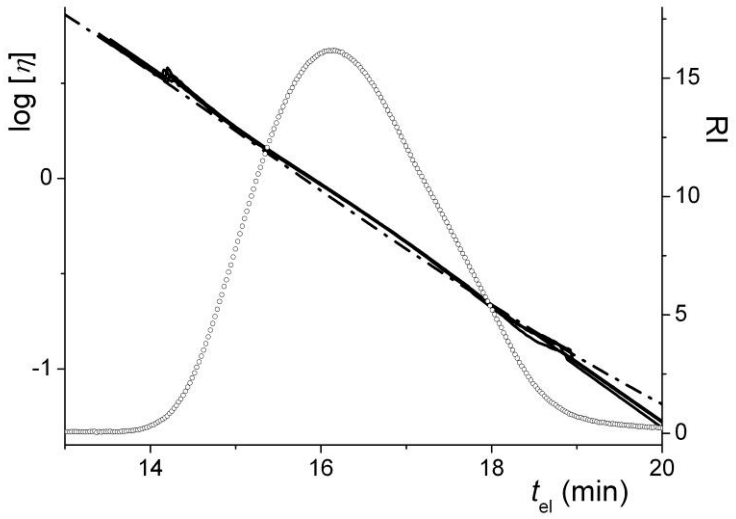

Fig. 6. Intrinsic viscosities (log [η]) against elution time (t_{el}) of PnBA obtained by universal calibration using Mark-Houwink-Sakurada parameters (dashed dotted line) and online viscometer (solid black line). The SEC chromatogram given by the refractive index detector (RI) is shown as a function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

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 paramaters 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 paramaters 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.

Comparison of the intrinsinc 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 wether 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 [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 (figure 5a of [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 refracrive 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.

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

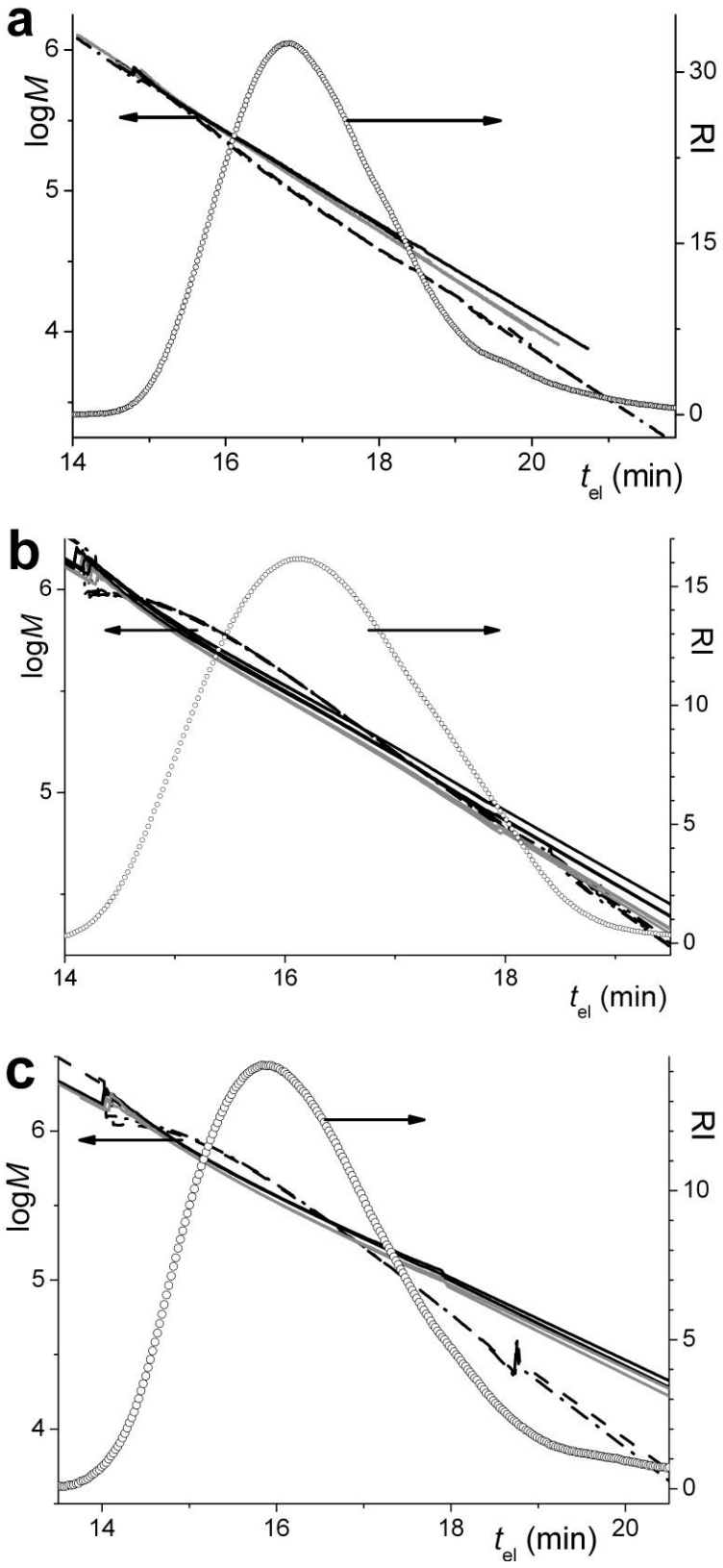

Fig. 7. Molecular weights (log *M*) obtained through universal calibration (dashed dotted line), triple detection (solid gray line) and low angle laser light scattering (solid black line)

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}.

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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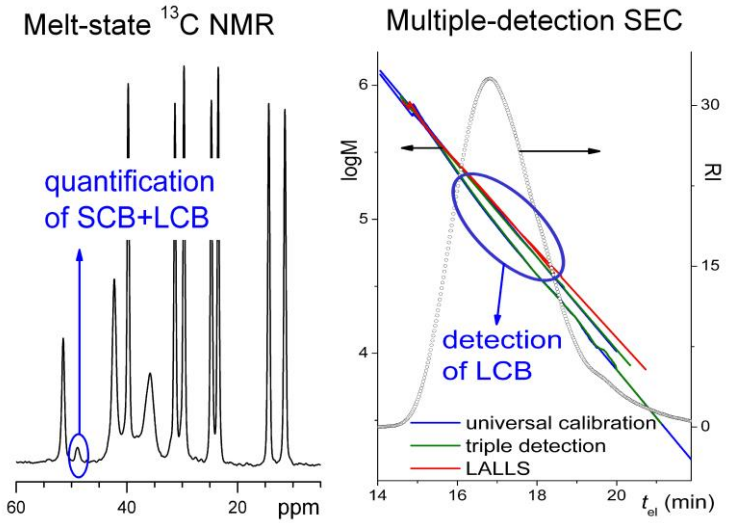
Graphical Abstract



Supporting Information for

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

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1. Tacticity of poly(n-alkyl acrylates)

For PMA, the different triads can be detected on the CH line at 41.3-41.6 ppm. Incomplete [1] and complete [2] assignments of the different triads can be found in the literature. For PEA, PBA and PHxA the different triads can be detected on the O-CH_2 line at 60.4-60.6 ppm for PEA, at 64.4-64.6 ppm for PBA and PHxA. The assignment can be found in the literature for PEA [1], PBA [2] and poly(pentyl acrylate) [3]. Since it is the same for PBA and poly(pentyl acrylate), it is assumed to be the same also for PBA and PHxA. The integration of the triad signals was done for the model PMA, PEA, PBA and PHxA. The representative examples of PMA and PHxA are given in Figure S1 and all the results are given in Table S1.

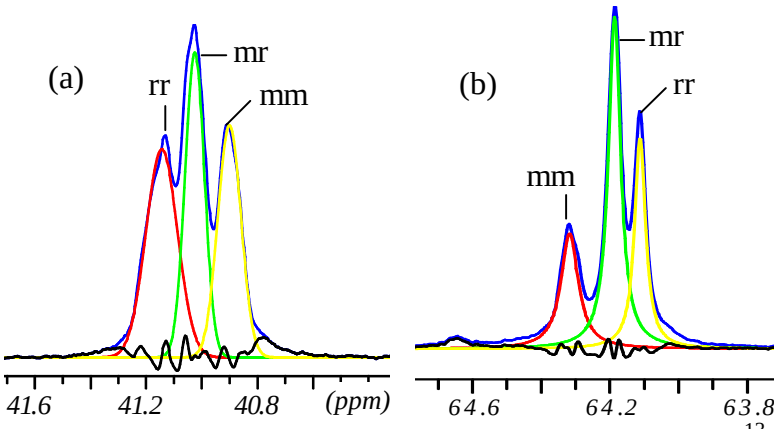


Fig. S1. Integration of triads signals for (a) PMA and (b) PHxA (^{13}C solution-state NMR spectra at 125.76 MHz in $CDCl_3$, at 29 and 33 °C); the curves in black are the recorded

spectrum and the difference of it and of the fitted lines; the curves in red, green and yellow are the fitted lines.

Table S1.
Tacticity of the model poly(n-alkyl acrylate) homopolymers.

Sample	δ (ppm)	Assignment	Content (%)	Tacticity
PMA	41.14	rr	36.8	atactic (tendency to syndio-
	41.02	mr	33.1	and isotacticity)
	40.90	mm	30.1	
PEA	60.37	rr	23.2	atactic
	60.23	mr	51.3	
	60.15	mm	25.5	
PBA	64.31	mm	20.8	atactic (slightly isotactic)
	64.18	mr	52.0	
	64.10	rr	27.2	
PHxA	64.32	mm	23.9	atactic
	64.19	mr	48.5	
	64.11	rr	27.6	

N.B.: The spectra were first recorded at a frequency of 75.47 MHz, but the signal-to-noise ratio (SNR) obtained in one week-end at 50 °C was sufficient to quantify only the tacticity, and not the branching level.

2. Synthesis and characterization of industrial copolymers

2.1. Emulsion polymerization

The samples were synthesized using a semi-batch (or semi-continuous) process. The polymerization is done using four different mixtures. The first one is an emulsion of surfactants and water, and is present from the beginning in the reactor (micelle diameter of several nm). The second one is a pre-emulsion composed of the monomers, surfactants and water (micelle diameter of a few nm). The two last ones are “initiator” solutions in water.
The radical polymerization itself consists of three steps. The synthesis of seeded particles (or nucleation) is first done in situ. Therefore, the two “initiator” solutions and a small part of the monomer pre-emulsion are added to the emulsion in the batch, and the polymerization is carried out. The reaction mixture at the beginning of this step consists of a continuous water phase and an emulsion of monomer droplets (of a few μm). The second step is the polymerization itself. It is carried out semi-continuously, by continuously adding the rest of the monomer pre-emulsion to the seeded particles emulsion, within a few hours. At the end of the polymerization, the particle diameter is of a few hundreds of nm. The polymer concentration is higher in the particles than in solution polymerization, so that the obtained polymer is expected to be more branched [4].
The third step is the polymerization of all the monomer residues. It takes place after all the pre-emulsion has been fed, and a waiting time is over. A post-polymerization initiator is added, which initiates the residual monomer in the polymer droplets and in the aqueous phase. This decreases the residual monomer amount to a value of a few ppm. This post-polymerization step is important for adhesive purpose (the monomer is a plasticizer that

decreases the cohesive strength of the PSA), as well as safety purpose (the acrylic monomers are highly toxic).

2.2. Expected copolymer structure

In free-radical emulsion copolymerization, the homogeneity of the monomer sequences along the polymer chains depends on the reactivity ratios and the relative water solubilities of the monomers, as well as on the type of polymerization process employed [5]. The microstructure of the polymer can not be determined using reactivity ratios, since they have not been determined for 2EHA/MA, MA/AA or 2EHA/AA pairs and they are only experimental fitting parameters, which can be used only for the pair of monomers on which they were determined [6-9]. The water solubilities of the three comonomers are however known and very different (s. Table S2), therefore the polymerization tends to be heterogeneous: AA is partitioned between the aqueous and the polymer phase, while 2EHA and MA are located almost only in the latter one. Furthermore, since the initiator is water soluble, the initiation and the first steps of propagation occur in the aqueous phase, so that the monomeric units located at the end of the polymer chains are preferentially AA, and then MA.

Table S2.
Solubility of the involved monomers in water.

Monomer	Water solubility (g of monomer per 100 g of water)	Ref.
2EHA	0.01	[10]
MA	5.2	[11]
AA	Infinite	[12]

The polymerization process implies the most homogeneous possible copolymerization: it is a semi-continuous process, under monomer-starved conditions. Consequently, a statistical copolymer is expected. Furthermore, with this process, the monomer concentration is low in the particles during the polymerization, while the polymer concentration is high. Thus it promotes a high degree of inter-or intramolecular transfer to the already formed polymer, resulting in a branched polymer structure [13]: we expect a branching level of a few percents of the monomeric units.
Finally, branched statistical copolymers are expected, with possibly a higher density of AA monomeric units at the surface of the particles and at the end of the polymer chains.

2.3. Characterization of copolymers

The solid content was measured by gravimetry and the particle size by light scattering (see Table S3). The solid content of the latices was measured as follows: around 2 g of the latex sample were put in a 1 g aluminum shell, and dried at 100 °C under vacuum for 1 night. All masses were precisely weighted (precision: ± 0.01 g). Three measurements were done simultaneously, and the average value was calculated. The mean diameter of the particles in the latices were measured by light scattering on a Zetasizer 5000 (Malvern Instruments Ltd., Malvern, UK) with a cell ZET 5110. The dispersions were diluted in water, until a slightly turbid dispersion was obtained. The photomultiplier should indeed record between 50 and 140 kcounts.s^{-1} to reduce dead time problems, avoid multiple scattering and ensure sufficient sensitivity. The measurements were done at room

temperature, with an incident wavelength of 633 nm. The angle between the incident beam and the recorded scattered beam was 90°. For each measurement, 30 records were done and their average was calculated.

Table S3.
Solid content and particle size of the copolymer samples

Sample	Solid content	Mean particle diameter
Copo2EHA	56 %	260 ± 6 nm
Copo1	55 %	214 ± 6 nm
Copo2	55 %	210 ± 6 nm

The glass transition temperature (T_g) of the copolymers have been obtained using differential scanning calorimetry (DSC) on a Mettler Toledo Star System. The measurements were done at a nitrogen flow of 30 mL.min^{-1}, with the following temperature cycle: heating from –100 °C to 150 °C at 10 °C.min^{-1}, then cooling from 150 °C to –100 °C at 10 °C.min^{-1}, and finally heating from –100 °C to 150 °C at 10 °C.min^{-1}. The first heating and cooling steps are used to erase the thermal history of the sample and detect evaporation of little molecules possibly trapped in the samples. The measurements were done on the second heating step. Their results are shown in Table S4. Only one T_g is detected for each sample, which is in accordance with the expected statistical character of the copolymers.

Table S4.
T_g of the copolymer samples, measured with DSC at 10 K.min^{-1}.

Sample	T_g	ΔC_p (J.g^{-1}.K^{-1})
Copo2EHA	213 K (-60 °C)	0.35
Copo1	225 K (-48 °C)	0.35
Copo2	226 K (-47 °C)	0.35

A first order endothermic peak is observed around 40 °C for the sample Copo2EHA. It is in fact the superposition of the melting peaks of the anionic and non-ionic surfactants, respectively located at 39 and 45 °C. They probably correspond to the crystallization of the oligo(ethylene oxide) units (as a comparison, pure high molar mass poly(ethylene oxide), PEO, exhibits a melting point of 65 °C). These values were measured on pure surfactants samples (available as aqueous solutions, which were freeze-dried), using the same temperature cycle as for the polymer samples. It should be noted that this peak is seen only for the homopolymer of 2EHA, which has the lowest T_g. Furthermore, this peak is clearly seen even if the total amount of surfactants is 1 wt%, since the first order transitions (e.g. melting) are more energetic than the second order ones (e.g. glass transition).

The measured T_g of 2EHA falls within the range of literature values, which are varying from 188 K (dilatometry [5]) to 223 K [10, 14], depending on the method used for the measurement. A value of 215 K measured by DSC at 20 K.min^{-1} has been reported [15], which is in accordance with the value reported here. The T_g of a copolymer of two monomers A and B can be approximately calculated from several equations [16], of which the probably most well known is the Fox-equation [17]:

$$\frac{1}{Tg} = \frac{w_A}{Tg_A} + \frac{w_B}{Tg_B}$$

where w_A and w_B are the mass fractions of the monomeric units A and B, Tg_A and Tg_B are the respective glass transition temperatures of the corresponding homopolymers in Kelvin. The glass transition temperatures of the involved comonomers are given in Table S5.

Table S5.
Glass transition temperatures of the involved comonomers, measured with DSC at 20 K.min^{-1}.[15]

Homopolymer	T_g
poly(2-ethylhexyl acrylate)	215 K (-58 °C)
poly(methyl acrylate)	295 K (22 °C)
poly(acrylic acid)	403 K (130 °C)

A statistical copolymer of 80 % of 2EHA with 20 % MA would have a T_g of:

$$\frac{1}{Tg}=\frac{w_{2EHA}}{Tg_{2EHA}}+\frac{w_{MA}}{Tg_{MA}}=\frac{0.8}{215}+\frac{0.2}{295}=0.004399, \quad \text{thus } T_g = 227K \qquad (-46 \quad °C)$$

which is in agreement with the measured values. All the measured T_g values are in good agreement with the values found in the literature.

Films were cast from the latex samples on microscope object slides. Only new object slides were used, and washed twice with ethanol and twice with acetone beforehand, in order to eliminate grease. Some latex sample was then put on the surface and spread with a spatula. During the first trial, the samples were left 50 minutes in the room, until the film became transparent, then dried 1 night at 80 °C under vacuum, and then left in the room again. These films were slightly yellow and considered as having been somehow degraded in the oven. Therefore we chose to let the samples dry at room temperature for at least seven days; weighting and DSC proved that they were dry.

3. Additional information about NMR measurements

3.1. Determination of chemical shifts of surfactants and solvents

Solution-state NMR was used to determine the chemical shifts of the surfactants present in the studied samples (Figure S2). The assignment of all the observed lines is given in the Table S6.

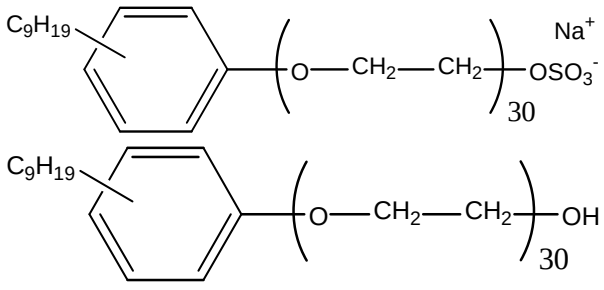


Fig. S2. Chemical formulae of the surfactants

Table S6.
^{13}C chemical shifts of the surfactants used in the synthesis of the copolymer samples.

δ (ppm)	Intensity (%)	Assignment
10 to 40	12	alkyl group C_9H_{19}
72	80	ethoxy chain –(CH_2-CH_2-O)-
116, 129, 143 and 158	8	aromatic ring

The chemical shifts of the crosslinker are known but are confidential.

The different chemical shifts of the solvents used in the experiments can be found in the literature and are summarized in the Table S7.

Table S7.
^{13}C chemical shifts of the solvents used in the NMR experiments.

Solvent	δ (ppm)	Assignment
$CDCl_3$	77.2	$CDCl_3$
$C_2D_2Cl_4$	73.8	$C_2D_2Cl_4$
DMF-d_7	29.8 and 34.9	methyl groups
	163.2	aldehyde group
THF-d_8	25.4	CH_2 group in β from O
	67.6	CH_2 group in α from O

3.2. Full ^{13}C chemical shift assignment for 2EHA, MA and AA monomeric units

The ^{13}C chemical shifts of the different nuclei of 2EHA, MA and AA monomeric units have been assigned by comparison of the measured values with calculated values (from incremental calculations [18]) and with values from the literature [2, 19, 20] (s. tables S8 and S9 and Figure S3 for the identification of the carbon atoms).

Table S8.
Assignment of the ^{13}C chemical shifts of MA and AA monomeric units.

Monomeric unit	δ (ppm) in copolymers (measured)	Assignment		δ (ppm) in homopolymers (calculated)	δ (ppm) in homopolymers (literature) [2]
MA	35.7 to 36.9	12	CH_2	24 to 25	34.5 to 35.9
	42.2	13	CH	40	41.3 to 41.6
	51.7	15	O-CH_3	48	51.5
	175.0	14	C=O		174.9
AA	35.9 to 36.7	16	CH_2	25	38.7 to 41.5
	42.2	17	CH	42	47.7-49.8
	175.0	18	C=O		187.3

Table S9.
Assignment of the ^{13}C chemical shifts of 2EHA monomeric units.

δ (ppm) in copolymers (measured)		Assignment	δ (ppm) in homopolymer (calculated) [18]	δ (ppm) in homopolymer (literature)[20]	δ (ppm) in homopolymer (literature) [19]
11.4	9	CH_3, side-group	11	10.3	14
14.5	11	CH_3, side-group	14	13.4	10.7
23.8	8	CH_2, side-group	23	22.6	23.0
24.5	10	CH_2, side-group	26	23.5	23.5
29.8	7	CH_2, side-group	30	28.6	28.9
31.2	6	CH_2, side-group	33	30.1	30.1
35.9 to 36.7	1	CH_2, backbone	24 to 25	34.8 to 35.6	33.5 to 37.3
39.6	5	CH, side-group	45	38.5	38.5
42.2	2	CH, backbone	40	41.2	41.5
48.5	2’	branched Cq, backbone	51	48.0	47.2 to 48.4
67 to 68	4	O-CH_2, side-group	71	66.0	66.9
172.6	3’	branched or terminal C=O		171.2	
175.0	3	C=O		173.5	174.3

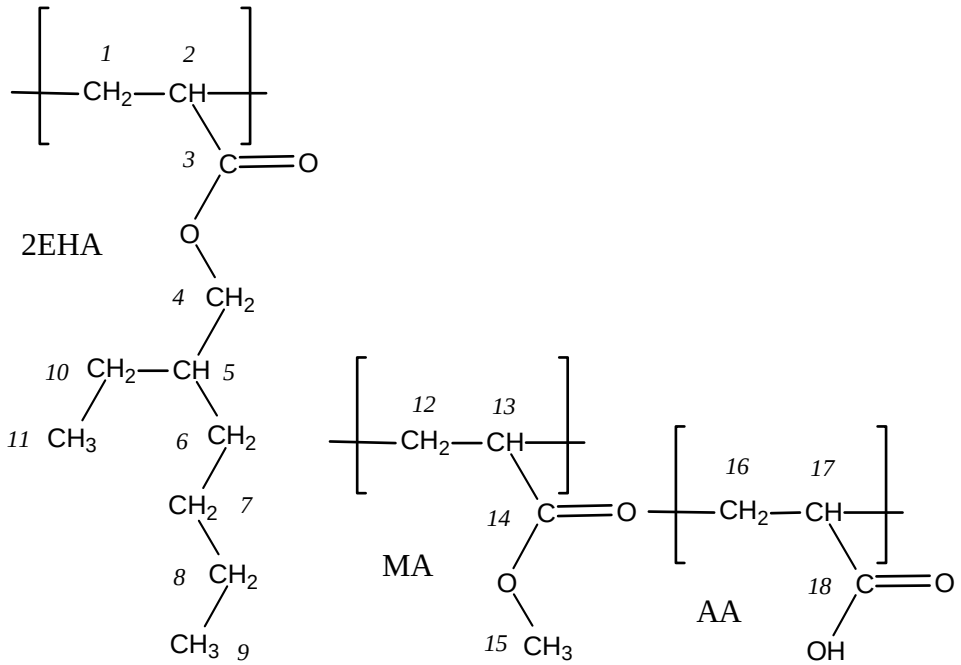
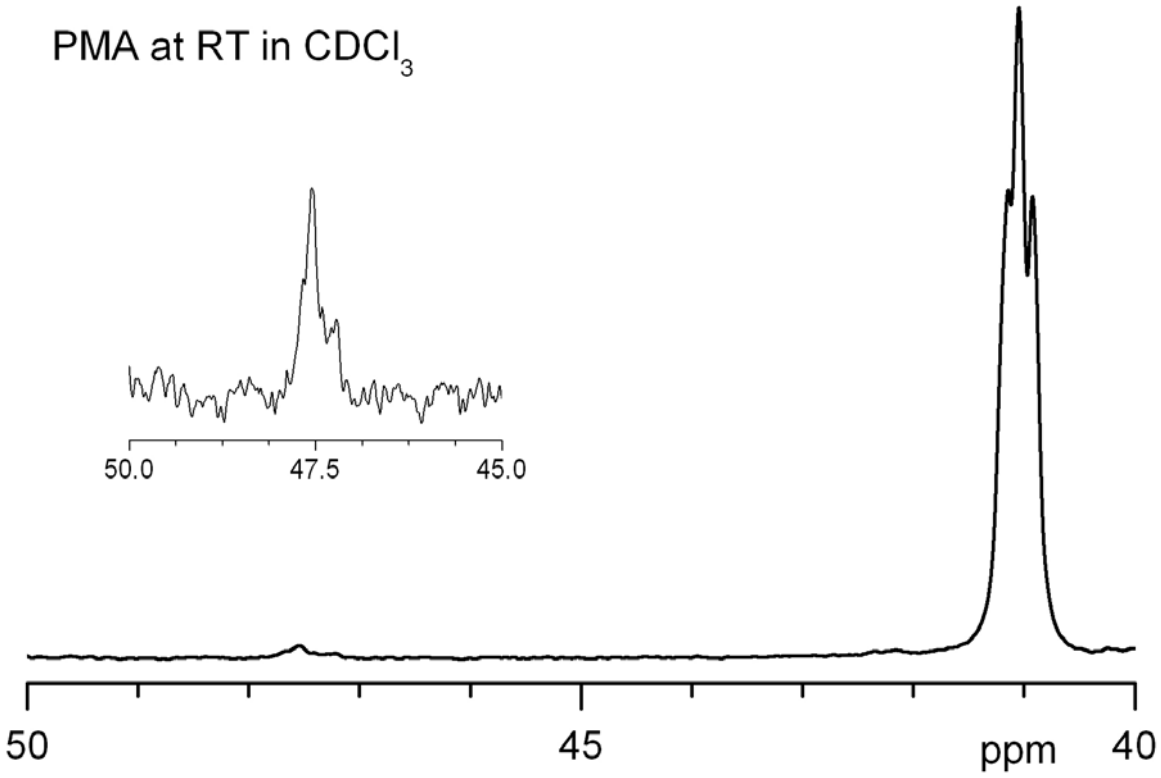
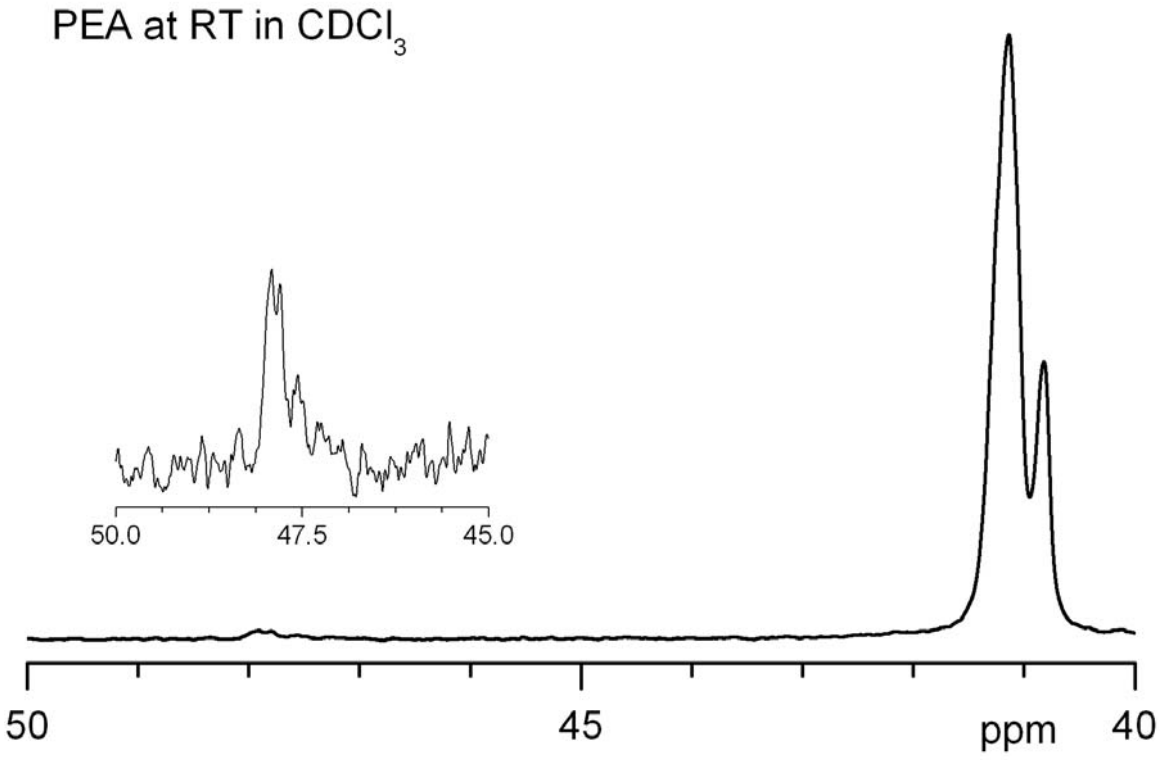
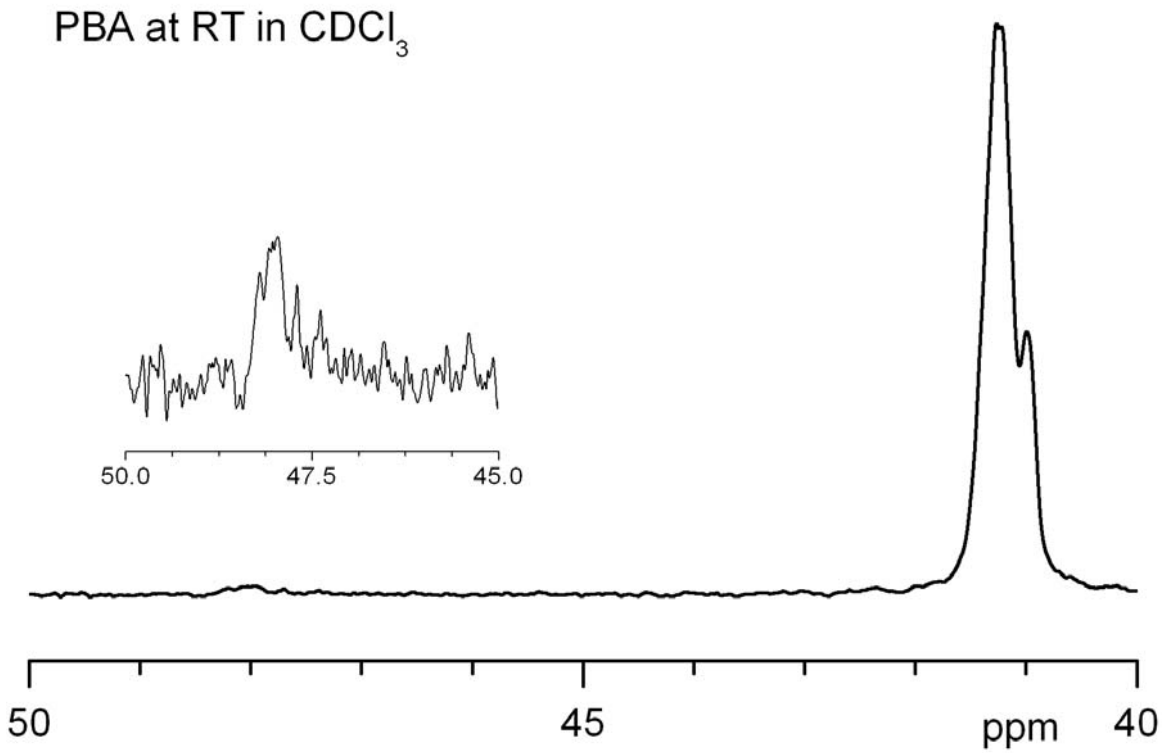


Fig. S3. Identification of the protons and carbons of the different monomeric units of the copolymer samples.

3.3. ^{13}C solution-state NMR spectra of poly(n-alkyl acrylates) and Copo2EHA



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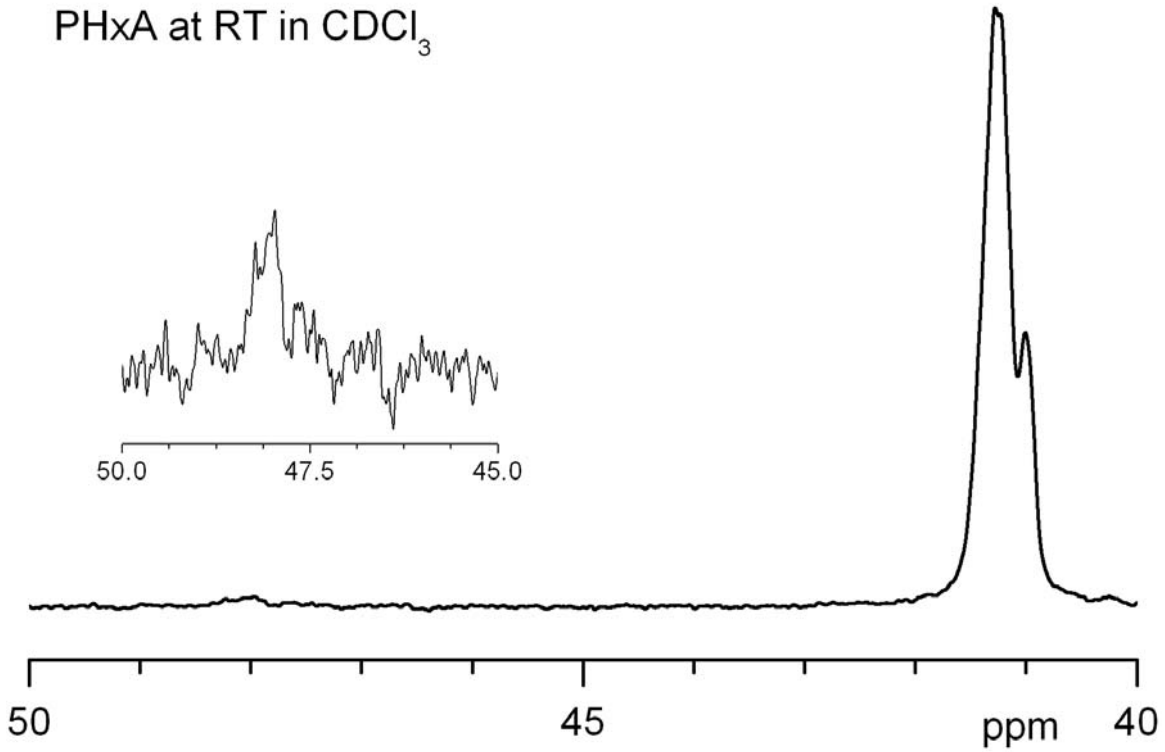
45.0
50
45
ppm
40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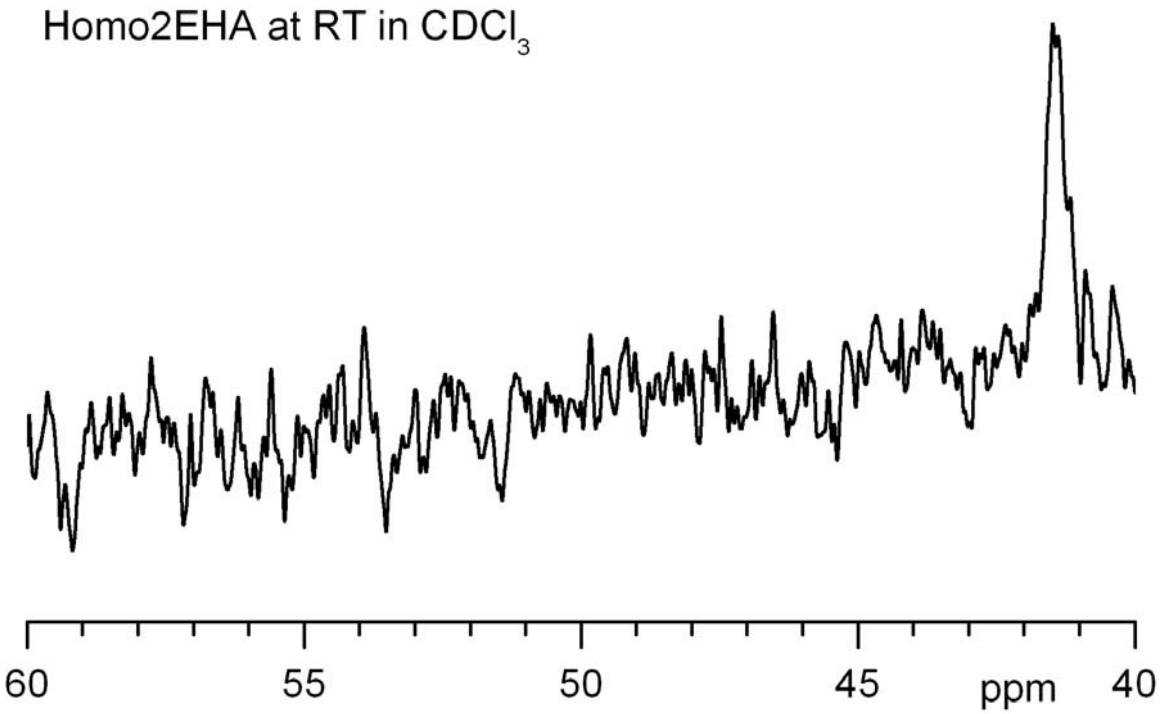
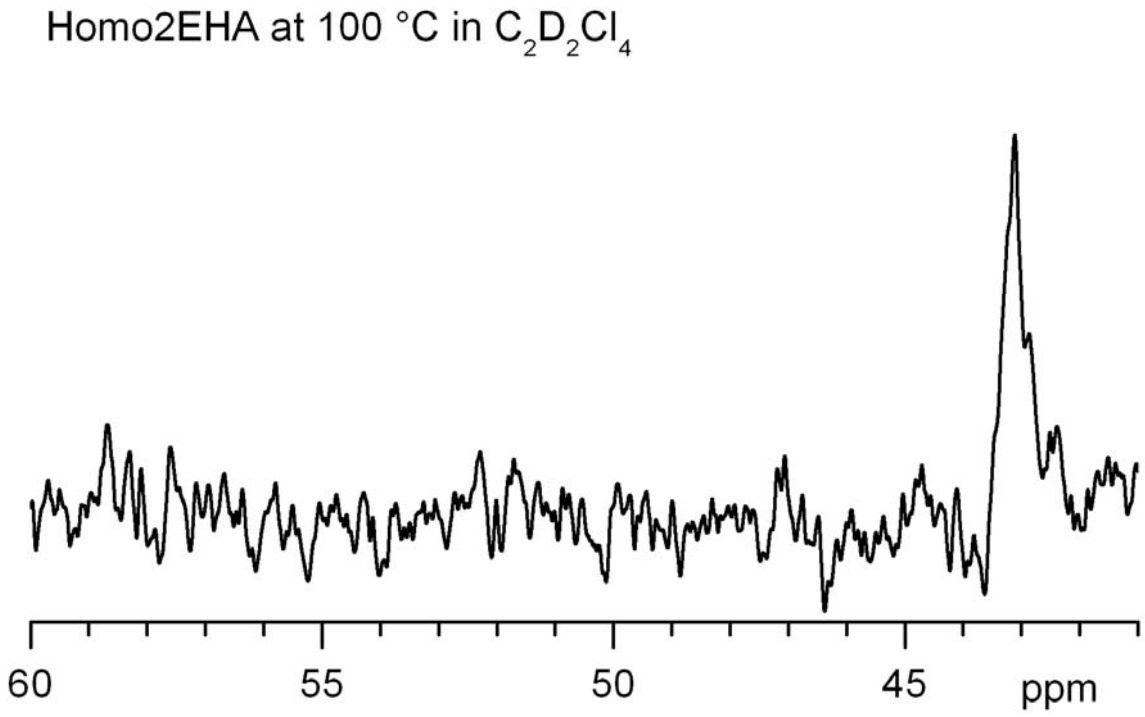
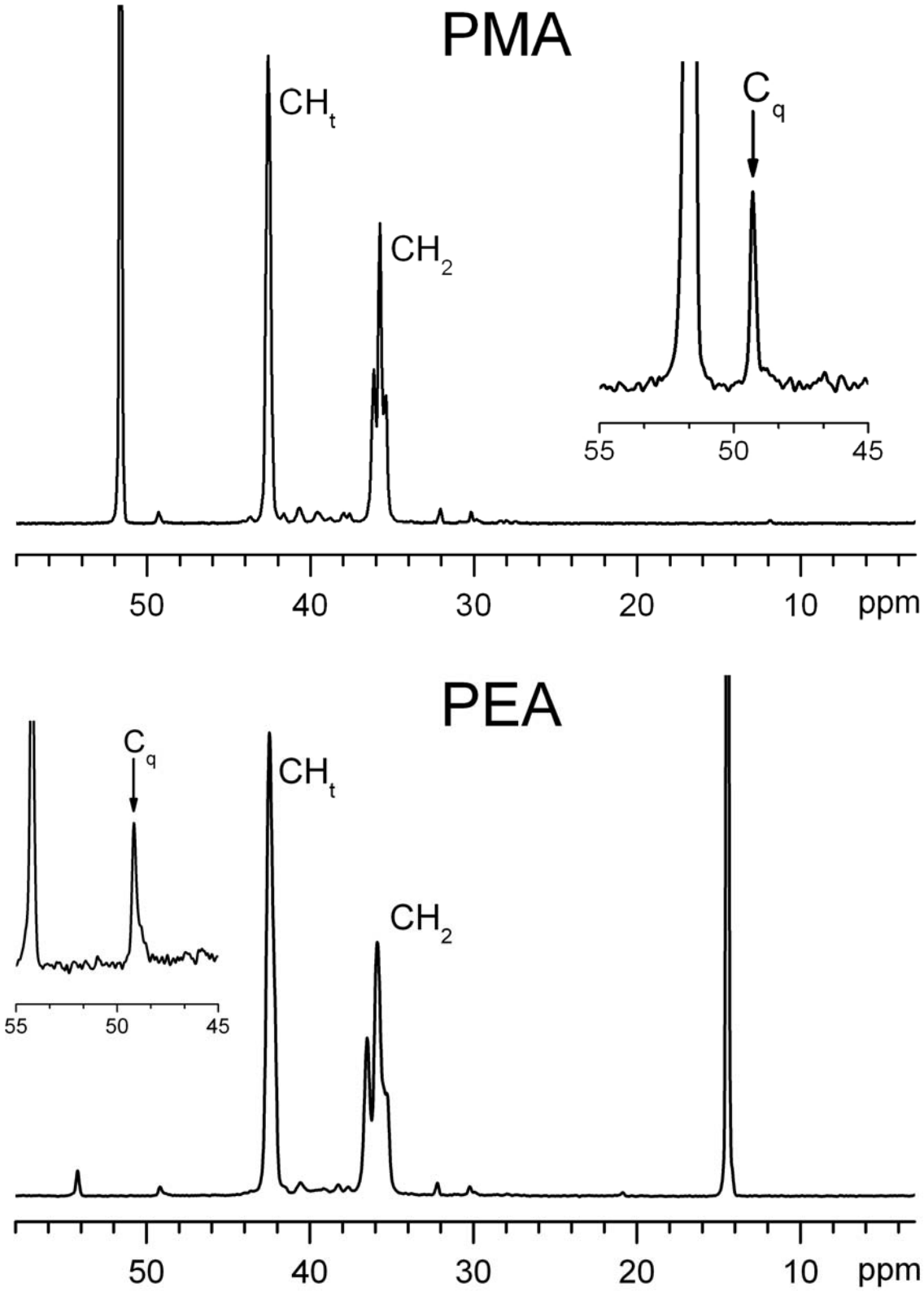
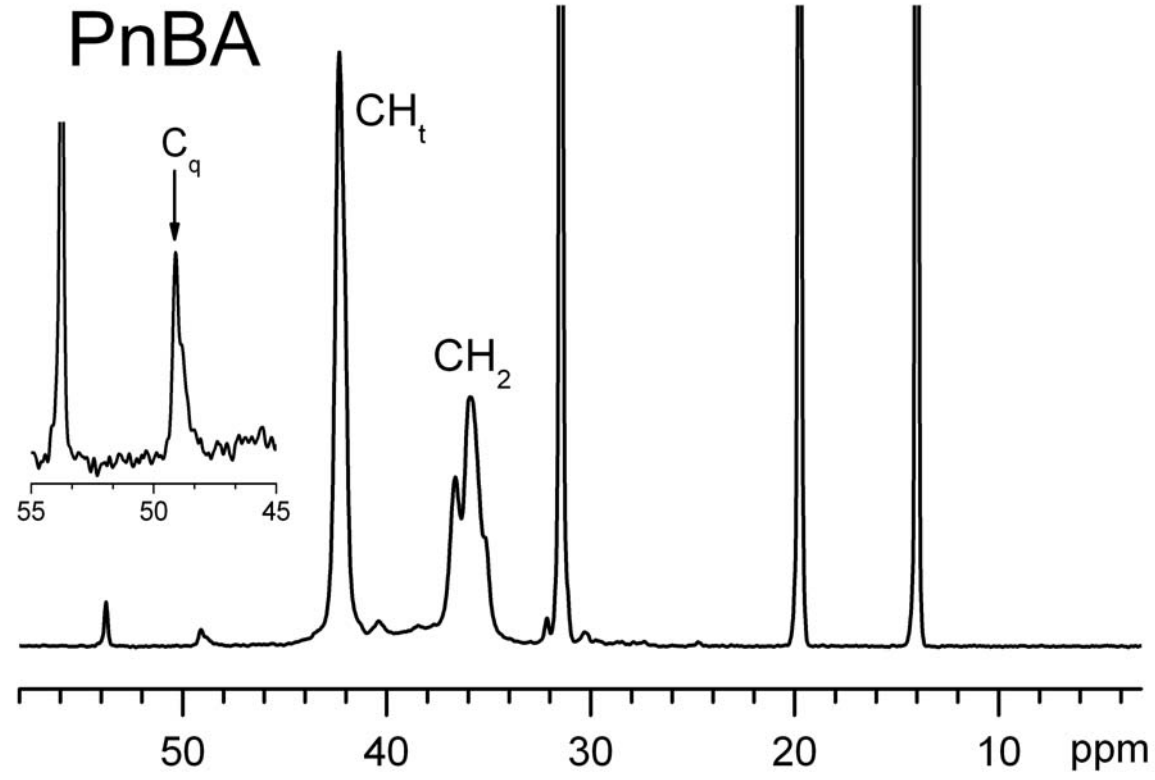
45.0
50
45
ppm
40


Homo2EHA at RT in $CDCl_3$
60
55
50
45
ppm
40


Homo2EHA at 100 °C in $C_2D_2Cl_4$
60
55
50
45
ppm

3.4. ^{13}C melt-state NMR spectra of poly(n-alkyl acrylates) and copolymers

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CH_t
CH_2
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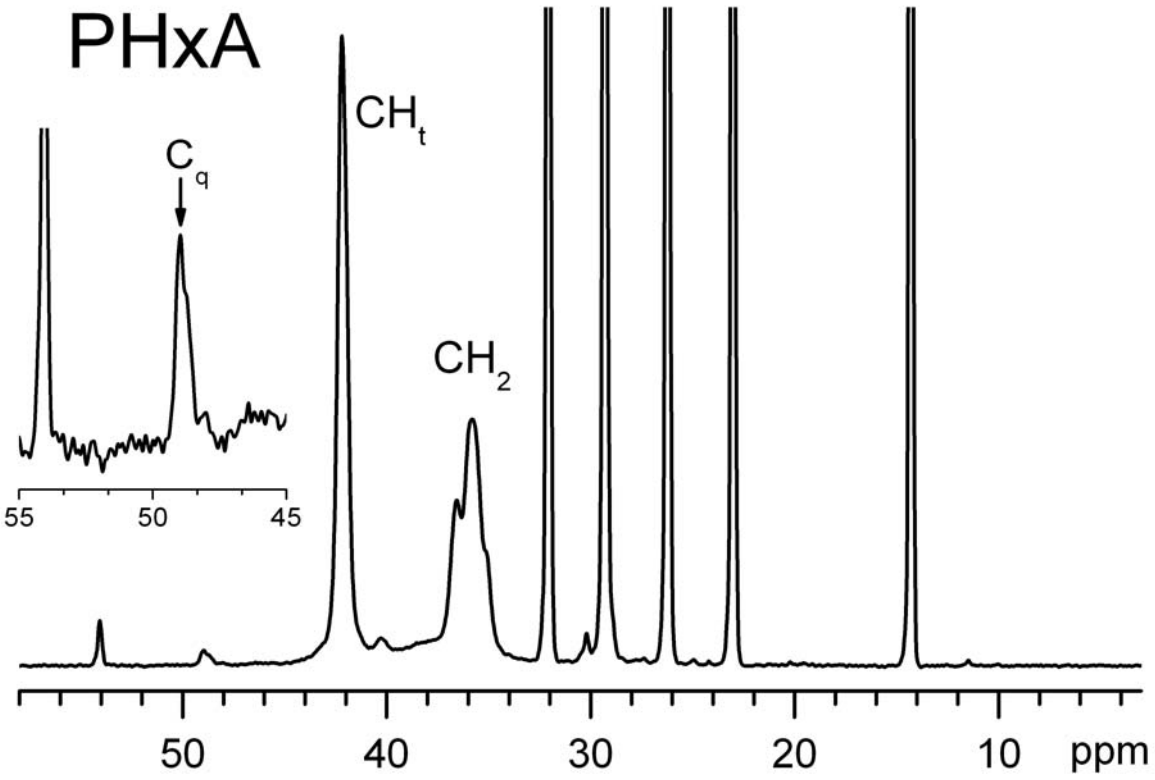
40
30
20
10
ppm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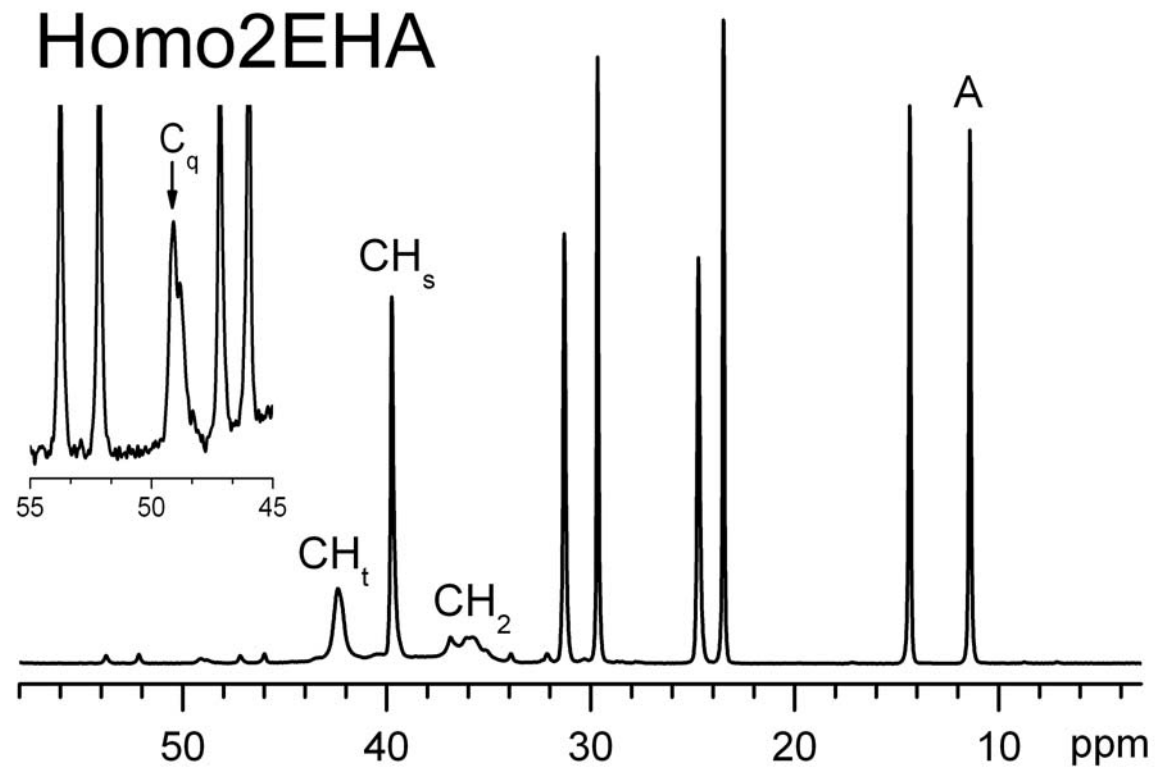
40
30
20
10
ppm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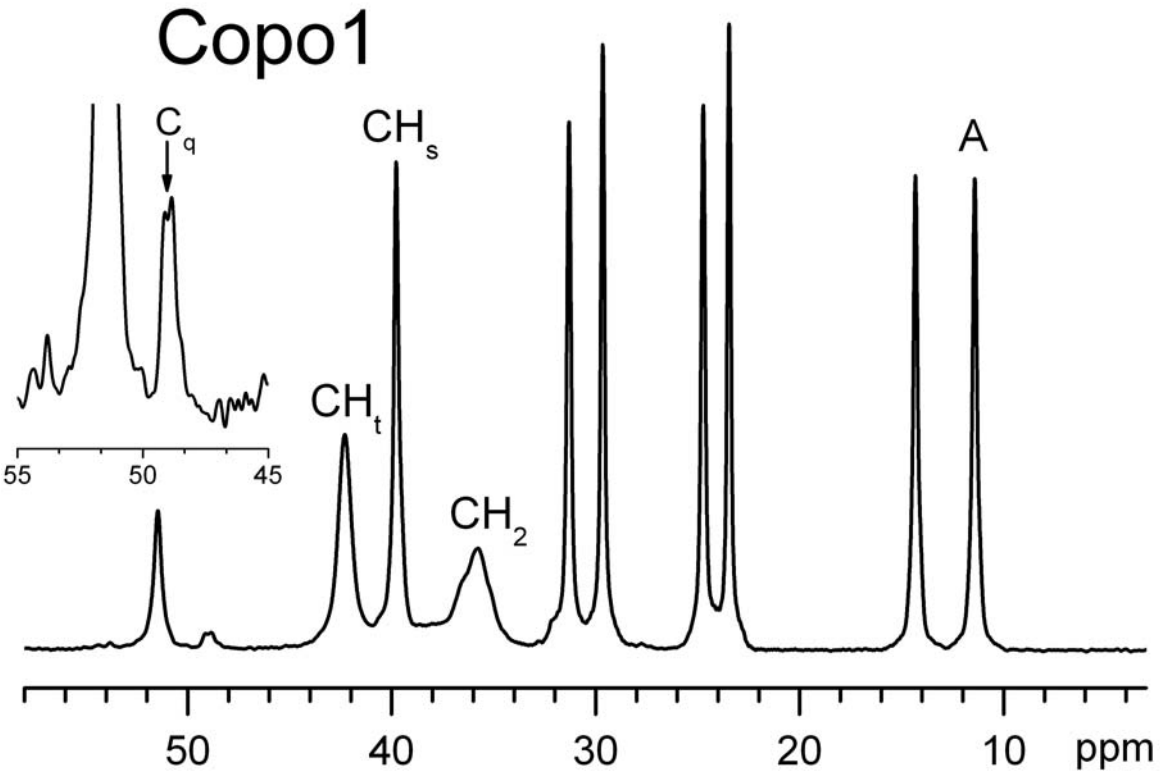
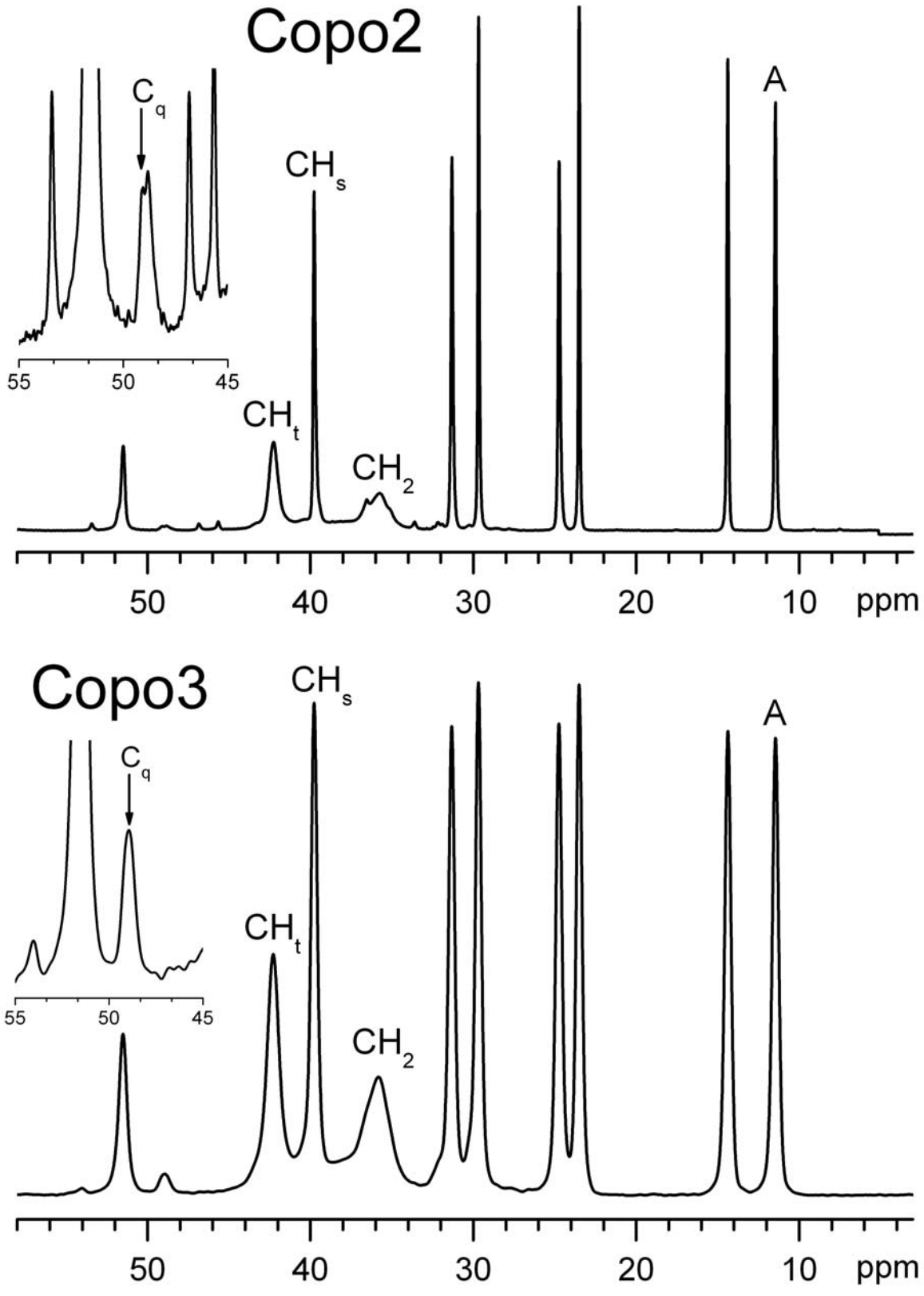
CH s
CH t
CH 2
A
55
50
45
50
40
30
20
10
ppm


Copo1
C q
CH s
CH t
CH 2
A
55
50
45
50
40
30
20
10
ppm


Copo2
C_q
CH_s
A
CH_t
CH_2
55
50
45
50
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30
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ppm
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A
C_q
CH_t
CH_2
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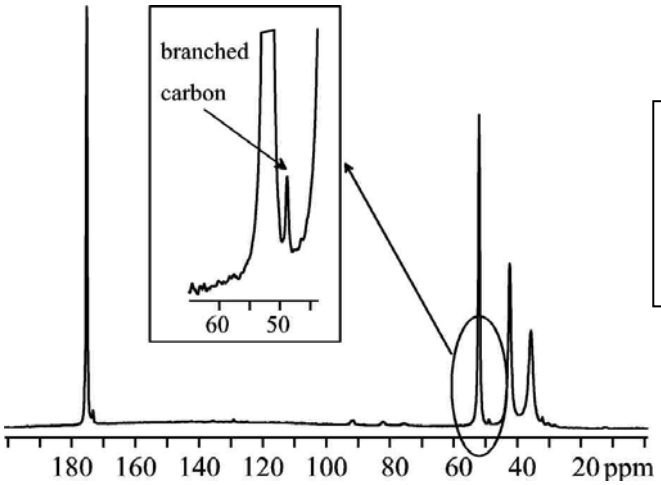
10
ppm



PMA, 75 MHz,
120 °C ~Tg+100 °C,
3 kHz MAS,
relaxation delay 10 s,
10240 transients

4. Integration ranges and integral values used for determination of degrees of branching

For copolymers, with melt-state NMR:

Sample	$I(C_q)$	$I(CH_t+ CH_2+ CH_s)$	$I(A)$	Δf_q	Δf_t	Δf_A
Copo2EHA	4.441	278.3	100	2.16	10.9	2.75
Copo1	7.352	370.3	100	2.23	12.0	4.12
Copo2	8.420	670.6	196.7	2.79	10.9	1.76
Copo3	16.66	703.1	190.4	2.50	14.5	4.00

For homopolymers:

Sample	melt-state NMR				solution-state NMR			
	$I(C_q)$	$I(CH_t+ CH_2)$	Δf_q	Δf_t	$I(C_q)$	$I(CH_t)$	Δf_q	Δf_t
PMA	1.92	196	2	12	2.12	979	2	3
PEA	3.25	488	2	12	1.58	984	2	3
PBA	5.35	474	2	12	2.29	971	2	3
PHxA	9.94	861	2	12	1.78	982	2	3

Integrals values I are given in arbitrary unit, and integration ranges Δf in ppm.

5. Additional information about SEC measurements: specific refractive index, d*n*/d*c*, values for polyacrylates in THF determined in this work or from the literature

Polymer	d*n*/d*c* ($L.g^{-1}$)	*T* (°C)	Number of samples (λ in nm)	MW range ($g.mol^{-1}$)	Determination method	Ref.
PAM	0.068 ± 0.002	25	6, 546	$M_w=5.10^4$ à 6.10^5	RDBP*	[21]
	0.063	30	1		SEC	This work
	0.06	30	1			
	0.067	30	1			
	0.075	30	1			
	0.062	30	1			
	0.068	30	1			
	0.071	40	1 (670)	PLP, high conversion		
	0.076	40	1 (670)			
PAtB	0.064 ± 0.002	25	5, 546	$M_w=10^5$ à 8.10^5	RDBP*	[21]
	0.063 ± 0.001	30	4		SEC	This work
	0.058	40	1, 670	PLP, high conversion	SEC	
	0.06	40	1, 670			

*RDBP is the Brice-Phoenix differential refractomer

6. Additional discussion about SEC measurements: validity of MHS parameters of polyacrylates

Mark-Houwink-Sakurada (MHS) parameters are widely used in SEC to determine molecular weight because single-detection SEC can then be used, instead of the more expensive and tedious multiple-detection one. However, discussion of the validity of MHS parameters is more important as usually considered in the literature. MHS relation is not always valid for short and very long polymer chains (see discussion and references in [22]). In the case of polyacrylates, MHS relation is not valid for all polyacrylates tested up to now but poly(n-butyl acrylate) because of the presence of long-chain branching (LCB) as discussed in [23] and in the main text.

The MHS values determined in this work for poly(2-ethylhexyl acrylate) (Table 5 of the main text) exhibit a surprisingly high K value: 130 $dL \cdot g^{-1}$. The α value is on the other hand low: 0.39. This may be partially explained by a higher level of LCB than in other P2EHA. This may also be partially explained by the fact that K and α values are not independent [24]. When a is underestimated, K is overestimated and vice-versa.

Different MHS values obtained in the literature can be compared by calculating the hydrodynamic volume yielded by the different values. These plots [25] show that one set of values [26] is not consistent compared to the literature in the case of poly(methyl acrylate) [21, 27] and poly(n-butyl acrylate) (table 5).

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