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*Acrylate copolymers*

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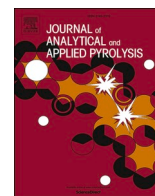
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## Expansion of the application range of pyrolysis-gas chromatography to copolymer sequence determination: Acrylate copolymers

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### ABSTRACT

The sequence distribution, which describes the order of monomers in a copolymer, is notoriously hard to study. The current standard in polymer sequence determination, NMR, is limited to simple copolymers due to lack in resolution and sensitivity. Therefore, an alternative method to determine the sequence of complex copolymers in the form of a developed pyrolysis-GC-MS method was investigated. Pyrolysis-GC-MS was applied to various acrylate copolymers; in the obtained pyrograms clear trimer distributions were observed and identified. Based on these results the sequence of these systems was calculated. The determined sequence values were found to be in line with expectations, demonstrating that the method was suitable for the sequence determination of binary acrylate copolymers. The developed method was also applied on various tertiary acrylate copolymers. Tertiary copolymers form many more distinct trimers rendering assignment more challenging. Nevertheless, based on a combination of chromatographic and mass spectrometric data, all formed trimers were assigned. To the best of our knowledge, this is the first time that a tertiary acrylate is sequenced by pyrolysis-GC.

### 1. Introduction

Synthetic polymers find wide application in daily life, with uses ranging from medical equipment and coatings to cosmetics and automotive parts. A polymer is not one defined molecule but rather a variety of molecules typically featuring distributions in chemical composition, molar mass, end groups, branching etc. One of these distributions is the sequence distribution which describes the order of monomers in a copolymer. With an increasing demand for polymers with specific properties, understanding the key factors that affect the properties of a material, including the sequence distribution, is of great importance [1–3].

The current standard for sequence determination is nuclear magnetic resonance (NMR) which has the advantage that it is absolutely quantitative. However, NMR suffers from major drawbacks such as limited sensitivity and poor spectroscopic resolution of different triad signals [4]. Furthermore, combinations of both tacticity and sequence can result in very complex and convoluted spectra, rendering sequence quantification very challenging or impossible [5–7]. Various researchers at

Nagoya University, mainly Tsuge, Okumoto, Nagaya, and Yamamoto et al. introduced pyrolysis-gas chromatography (Py-GC) as an alternative method [8–12]. During pyrolysis, dimers and trimers are formed which are indicative of the sequence in the original polymer [13,14]. Py-GC features advantages over NMR such as higher sensitivity and improved resolution between individual dimer and trimer species. The increased sensitivity has benefits such as allowing analysis of low amounts, like liquid chromatography fractions [15], or low abundant subunits, such as hybrid dimers/trimers in block copolymers. The increased resolution might enable the sequence determination of copolymers which feature very convoluted NMR spectra. Earlier work by the group of Tsuge and by Wang et al. was promising and provided solid results on various copolymer systems. The Py-GC method has seen little application since raising questions as to which extent the method is applicable to various copolymers as pyrolysis mechanisms and products vary widely per polymer [8–12,16]. Furthermore, the lack of reference material in literature limits the practical application to novel copolymer systems. The main drawback of Py-GC in copolymer sequence determination, is that not all polymers tend to form clear dimer and trimer

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**Table 1**

Polymer composition, molecular-weight distribution and polydispersity index information of the synthesized samples, including the composition determined by  $^1\text{H}$  NMR.

Sample	Copolymer composition mole- % based on synthesis recipe	$M_w$ (kDa)	$M_n$ (kDa)	PDI	mole- % MA	mole- % EA	mole- % BA
1	MA/EA 20/80	129	49	2.7	23	77	–
2	MA/EA 35/65	143	56	2.6	39	61	–
3	MA/EA 48/52	125	60	2.1	54	46	–
4	MA/EA 61/39	119	60	2.0	69	31	–
5	MA/EA 73/27	145	61	2.4	82	18	–
6	MA/BA 24/76	123	49	2.8	20	–	80
7	MA/BA 40/60	123	65	1.9	36	–	64
8	MA/BA 56/44	124	55	2.2	51	–	49
9	MA/BA 70/30	135	53	2.6	66	–	34
10	MA/BA 83/17	143	57	2.5	81	–	19
11	EA/BA 21/79	134	50	2.7	–	23	77
12	EA/BA 36/64	120	43	2.8	–	38	62
13	EA/BA 51/49	125	42	3.0	–	52	48
14	EA/BA 66/34	126	49	2.6	–	66	34
15	EA/BA 81/19	130	52	2.5	–	80	20
16	MA/EA/BA 33/33/33	118	45	2.6	31	33	36
17	MA/EA/BA 25/25/50	112	43	2.6	23	26	52
18	MA/EA/BA 25/50/25	54	30	1.8	22	52	26
19	MA/EA/BA 50/25/25	138	54	2.6	45	26	28

blocks upon pyrolysis. Indeed, some polymers undergo full depolymerization which renders the relation to the original sequence in the intact polymer more challenging [16]. Furthermore, the formed fragment might not be directly representative of the polymers sequence since the concentration of trimer formed is a product of the concentration in the polymer as well as its formation constant in pyrolysis. This concept was introduced as the boundary condition by Shibasaki [17]. The sequence calculation by Py-GC is performed using the same method as with NMR, typically the trimers are quantified and from their relative abundance the monomer number average sequence length (NASL) is determined as shown in Eq. 1a and b [18].

$$N_A = \frac{n_{AAA} + n_{AAB+BAA} + n_{BAB}}{1 + \frac{1}{2}n_{AAB+BAA} + n_{BAB}} \quad (1a)$$

$$N_B = \frac{n_{BBB} + n_{BBA+ABB} + n_{ABA}}{1 + \frac{1}{2}n_{BBA+ABB} + n_{ABA}} \quad (1b)$$

In which  $N_x$  indicates the NASL of a specific monomer and  $n_x$  the molar fraction of a trimer. Based on the calculated NASL values the degree of randomness ( $R$ ) can be determined (Eq. 2), which is a single value metric which indicates the degree of blockiness or the sequence. A perfect alternating polymer will have an  $R$  value of 2 and an ideal random copolymer will yield an  $R$  value of 1, a large block copolymer or a blend will feature an  $R$  value approaching 0.

$$R = \frac{1}{N_A} + \frac{1}{N_B} \quad (2)$$

Besides determination of the randomness the NASL of both monomers can also be used to calculate the polymer composition using Eq. 3 [14].

$$n_A = \frac{N_A}{N_A + N_B} \quad (3)$$

In which  $n_A$  indicates the molar fraction of monomer A. The determined NASL values can thus be used to calculate the copolymer composition, yielding more information on the chemical nature on the

sample.

In this paper, we demonstrate our developed Py-GC method to study the sequence of various acrylate copolymers. The sequence of these systems is challenging to study by NMR due to tacticity effects dominating the spectrum, to such a degree that sequencing by NMR has been unaccomplished so far. We assess the feasibility of sequence determination of binary systems, showcasing a strategy for assignment of the trimer signals. Furthermore, we expanded the method to tertiary acrylate systems, which to the best of our knowledge, have not been sequenced by either NMR or Py-GC.

## 2. Materials & methods

### 2.1. Chemicals

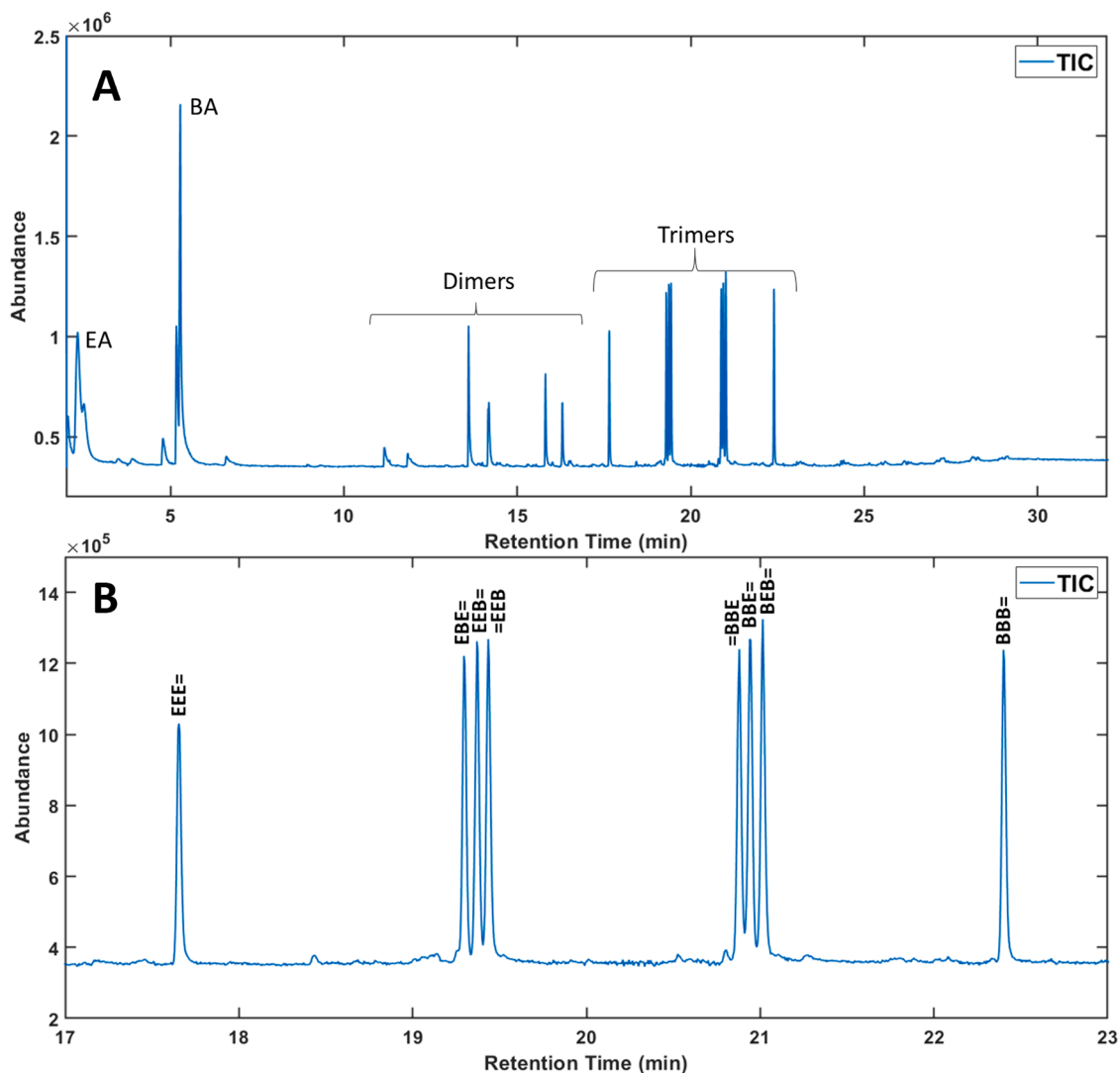
A set of acrylate copolymers was synthesized as follows. An initiator solution was made by dissolving 0.5 g 2,2'-azodi(2-methylbutyronitrile) (AIBN; Sigma Aldrich, Darmstadt, Germany) in 500 mL butanone (Acros organics, Geel, Belgium). Monomers were mixed in their respective amounts (Table 1 features an overview of synthesis recipes) up to a total mass of 2 g. Next, 3 mL initiator solution was added to this mixture. Monomers used were methyl acrylate (MA; Sigma Aldrich), ethyl acrylate (EA; Sigma Aldrich) butyl acrylate (BA; Sigma Aldrich). The samples were purged of oxygen with nitrogen and incubated at 70 °C for 3 h, under light mixing, and subsequently purged with compressed air to deactivate any remaining initiator and cooled to 4 °C. The cooled samples were then precipitated with a –20 °C 80/20 (v/v) methanol (Biosolve, Valkenswaard, the Netherlands) /water mixture after which the supernatant was removed, and the samples were allowed to dry at room temperature. In total five differing compositions of each copolymer were synthesized. A complete overview of the list of synthesized samples, including the determined molar mass averages and composition determined by size-exclusion chromatography (SEC) and nuclear magnetic resonance (NMR; conditions in section 2.2 and 2.4) can be found in Table 1.

### 2.2. Size-exclusion chromatography

Size-exclusion chromatography (SEC) was performed on an Agilent (Waldbronn, Germany) 1100 series LC system consisting of a quaternary pump coupled to an autosampler, a variable wavelength detector and a refractive index detector, which were used for detection in series. The separation was performed on two PLgel mixed-B columns (300 × 7.5 mm i.d., 10 μm particle size; Agilent). The flowrate was set to 1 mL·min<sup>-1</sup>, unstabilized THF (VWR, Amsterdam, the Netherlands) was used as eluent. 20 μL (corresponding to approximately 100 μg) of sample was injected. The MMD (molar mass distribution) was determined relatively to a set of 12 polystyrene standards (PSS, Mainz, Germany) with peak molar masses ( $M_p$ ) ranging from 682 to 2520,000 Da (PSS).

### 2.3. Pyrolysis gas chromatography mass spectrometry (Py-GC-MS)

A Shimadzu ('s-Hertogenbosch, The Netherlands) 2010 GC-MS coupled to an OPTIC-3 PTV (programmed temperature vaporizer; GL-Sciences, Eindhoven, The Netherlands) was used for Py-GC analysis of the synthesized samples. In brief the pyrolyzer consist of a sintered glass GC liner heated through resistive heating. The samples were injected at 40 °C at which the temperature was kept for 10 s after which the temperature was ramped (30 °C/s) to 120 °C and maintained to evaporate the solvent. After 2 min the temperature was ramped (30 °C/s) to 500 °C at which pyrolysis was performed for 2 min. After pyrolysis the PTV was kept at 300 °C for the rest of the run. The pyrolysate was separated on a RESTEK (Bellefonte, PA, USA) Rxi-5 ms column (5 % phenyl, 95 % diphenyl dimethyl polysiloxane, 30 m x 0.25 mm ID, film thickness: 0.25 μm). The GC temperature program started at 40 °C for 3 min after which the temperature was increased with 10 °C·min<sup>-1</sup> to 300 °C after



**Fig. 1.** A: Pyrogram of an EA-BA statistical copolymer which containing 52 % (mol/mol) EA (sample 13, Table 1) B: Detailed view of the trimer region of the pyrogram here E and B refer to the EA and BA residues respectively, = is used to indicate the location of the double bond.

which the temperature was maintained for 6 min. The column flow was set at  $1.7 \text{ mL}\cdot\text{min}^{-1}$  and the split ratio was set at 1:200 with helium as the carrier gas. Detection was conducted using electron ionization (EI) MS at an ionization energy of 70 eV. A full scan method was used that measures ions with  $m/z$  40 – 700 with event time 0.30 s starting after 2 min until the end of the GC-method. Approximately 10 mg of dried sample was dissolved in 2 mL unstabilized THF (VWR), 5  $\mu\text{L}$  of which was injected for analysis.

#### 2.4. NMR

$^1\text{H}$  NMR spectra were recorded on a Bruker (Rheinstetten, Germany) Avance NEO 500 MHz in deuterated chloroform ( $\text{CDCl}_3$ , Sigma Aldrich) at 298 K. Approximately 10–20 mg of sample was weighed in and dissolved in 0.7 mL  $\text{CDCl}_3$ . A pulse delay of 5 s was applied between scans, in total of 32 scans were recorded. The acquisition time was set at 2.7 s, the digital resolution was 0.37 Hz and the flip angle was  $90^\circ$ .

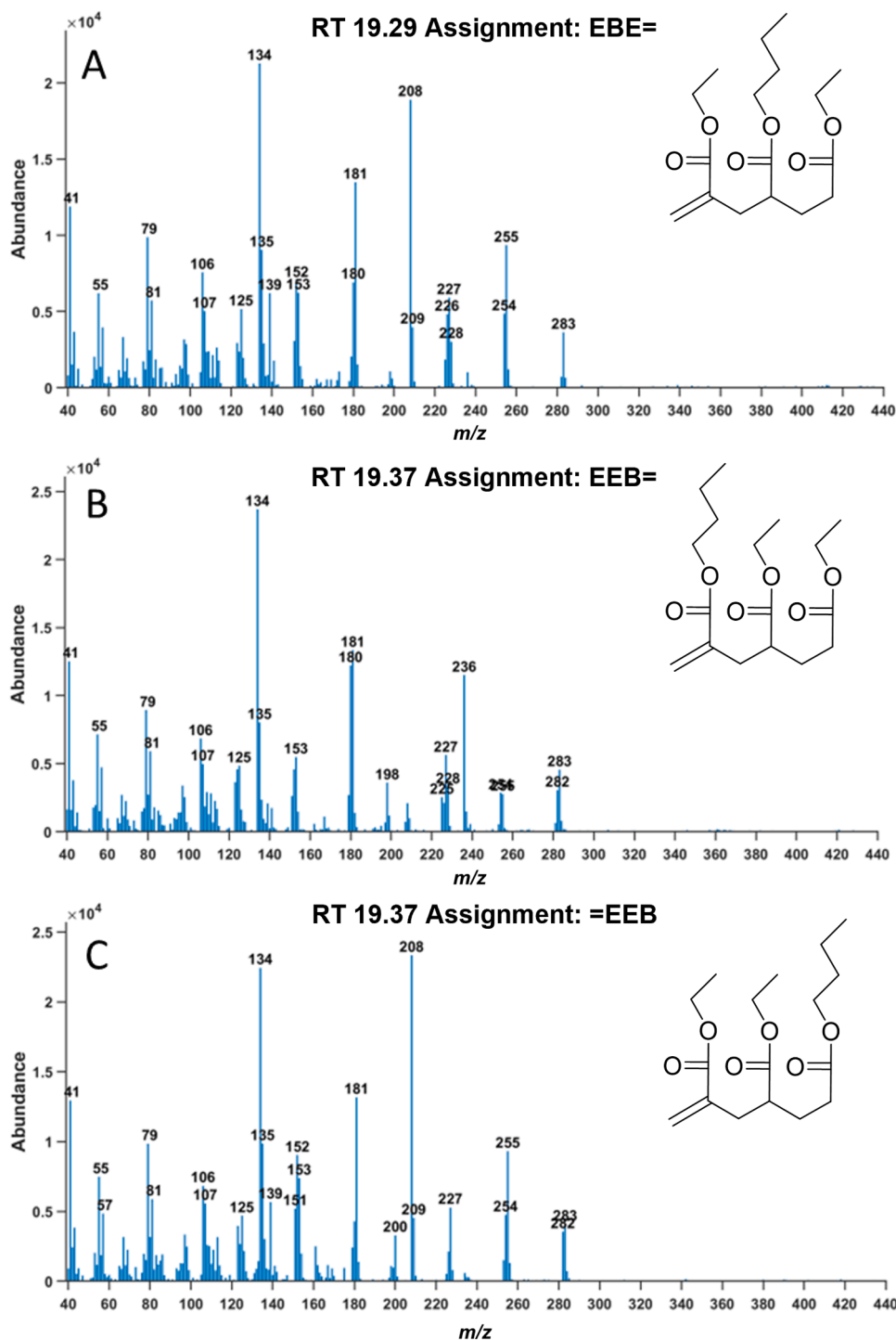
### 3. Results & discussion

#### 3.1. Binary copolymers

A set of acrylate copolymers (MA-EA, EA-BA and MA-BA, Table 1,

samples 1–15) was synthesized to assess the feasibility of sequencing them with Py-GC. The synthesized samples were subjected to size-exclusion chromatography (SEC) to confirm polymerization and determine the MMD and PDI (polydispersity index). Since the determined sequence is influenced by the composition,  $^1\text{H}$  NMR spectra were recorded of all copolymers to confirm the composition. The determined MMD and PDI as determined by SEC, as well as the composition determined by  $^1\text{H}$  NMR can be found in Table 1.

The synthesized copolymers were subjected to Py-GC analysis, yielding clear trimer signals which were used for sequence analysis. The assignment of trimers is challenging due to mass-spectral similarities, accurate assignment is crucial to obtaining accurate sequence information, however. Due to the limited literature on Py-GC for copolymer sequence determination there is little reference material for identification of the formed trimers. Therefore, we describe our approach to the assignment of the trimers in various copolymers as it might aid others in the application of Py-GC to polymer sequence determination. The trimers were assigned based on retention time and mass spectrometric data, where available reference pyrograms were consulted [16]. A typical pyrogram of an EA-BA copolymer (sample 13, Table 1) can be seen in Fig. 1A. The observed trimer region ( $t_R = 17\text{--}23$  min) containing the sequence information can be seen in Fig. 1B. To obtain sequence information all trimer signals must be assigned and integrated, after which



**Fig. 2.** : Mass spectra of the EBE (2A), EEB= (2B) and =EBB (2C) trimer, E and B indicate an EA or BA monomer respectively, = indicates the location of the double bond.

Eq. 1a and b can be applied to calculate the sequence of the system.

Assignment of the pure EA and BA trimers was performed based on assignment of the homopolymers. The two sets of three signals in between can then be attributed to trimers containing one BA and two EA monomers ( $t_R = 19.4$  min) and two BA and one EA monomer ( $t_R = 21$  min) based on boiling point. The reason for the three signals can be explained by the three forms of trimer for each monomer compositions. If we consider the first cluster of three peaks at  $t_R = 19.4$  min, which consist of two EA monomers and one BA monomer we can form an EEB (in which E and B indicate an EA and BA residue respectively) and an

EBE trimer, the former can feature two forms yielding separate signals since the double bond can be on the BA or EA monomer. Typically, the monomer in the middle contributes less retention in the elution of the EBE trimer before the two forms of the EEB trimer [19]. This can be supported by the MS spectra of the different trimers, if we examine the MS spectra of the three trimers (Fig. 2 A-C) containing two EA residues and one BA residue, we see that  $m/z$  236 and 208 are indicative of the location of the double bond being on BA or EA respectively. We propose that these fragments form through a mechanism of double alcohol loss, by means of a hydrogen transfer, which cannot occur on the

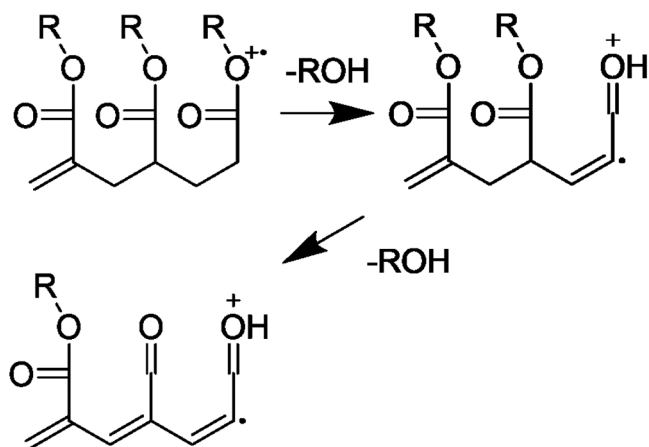


Fig. 3. Proposed reaction scheme for the observed double alcohol loss in acrylate trimers.

side of the double bond due to a lack of a hydrogen atom on that side. Double alcohol loss has been observed before in acrylate trimers [20]. The proposal of this rearrangement is outlined in Fig. 3, structures for all formed fragments can be seen in Supplementary Fig. S1, MS spectra of all formed trimers are given in Supplementary Figs. S7–29 [21].

The peak areas of the assigned trimer signals were directly used in Eqs. 1a and 1b from which the randomness could be determined using Eq. 2, yielding NASL values close to two, as can be expected for a polymer with this composition featuring random character. The full results featuring in the determined sequence lengths and randomness for all binary samples can be seen in Fig. 5 at the end of this section. The MA-BA (full chromatogram and zoom in of the trimer region in Supplementary Figs. S2 and S3) system was assigned using the same method. Only it should be noted that the MA trimer overlapped with a BA dimer (Supplementary Fig. S4). Analysis of the pyrograms and MS spectra of the homopolymers revealed that the  $m/z$  134 fragment is selective for the MA trimer, the EIC (extracted ion current) of this mass was then used to calculate the TIC area contribution of the MA trimer peak in the pyrogram of the copolymer. The EA-MA (Fig. 4, for a full pyrogram see Supplementary Fig. S5) pyrogram featured some overlapping signals. The MEM and MME= trimer seem to overlap based on the relative peak intensities and the lack of three distinct signals. This can be confirmed based on the extracted ion chromatograms (EIC) of  $m/z$  194 and  $m/z$  208 which are specific for the double bond being on an MA and EA respectively, as explained above.

As can be seen in Fig. 4 there are clearly two sets of overlapping signals at  $t_R = 16.4$  and  $17.1$  min. Since the  $m/z$  194 and  $m/z$  208 signals indicate the location of the double bond, the peaks can still be readily assigned, however. As can be seen both hybrid peak clusters feature three distinct trimer species, the cluster containing two MA monomers and one EA monomer features in order of retention the MEM, the MME= and the =MME trimers, where the = indicates the location of the double bond. The overlapping peaks were deconvoluted based on the assumption that the intensity of the two MME trimers is equal, the same method was used to deconvolute overlapping EEM= and EME signals for sequence calculations. With the assignment of all acrylate copolymers complete, the peak areas per trimer were determined in all samples (Table 1) and compared. The calculated NASL and randomness (R) of the acrylate copolymers, calculated using Eqs. 1 and 2, is outlined in Fig. 5.

As can be seen in Fig. 5 the randomness of all systems is close to one at all compositions indicating that the polymers are random. This was expected since the reaction constants of both monomers are similar [22]. This can also be observed by the clear correlation between the found sequence length and the expectations for a Bernoullian process (Transparent lines Fig. 5).

In this study the TIC peaks areas were used directly to calculate the NASL. The calculated NASL based on Py-GC with flame ionization detection (FID) corrected with effective carbon numbers are similar (Supplementary table 1), indicating that the MS signals are good indicators of concentration [23]. However, besides the detection efficiency the differences in the formation constant in the pyrolysis process can also cause misrepresentation of the determined trimer concentrations compared to the original polymer. Since all these systems were acrylates, we assume that pyrolysis mechanisms are relatively equal. The results represent this as the correlation between composition and sequence is evident and matches trends expected from a random copolymer. It should however be noted that since these systems feature no sequence sensitivity in  $^{13}\text{C}$  NMR the determined sequence values cannot be validated and should be considered semi-quantitative [7].

To further verify the determined values, the compositions were calculated using the determined NASL as they should reflect the determined composition. As can be seen in Fig. 6 there is a good agreement between the composition determined by NMR and the composition calculated using NASL values (Eq. 3), obtained by Py-GC. There are some minor systematic deviations, this is unsurprising however, since the composition determination via the determined NASL is very indirect compared to the NMR method. Nevertheless, the agreement between the data obtained using the two methods supports that the determined NASL values are accurate.

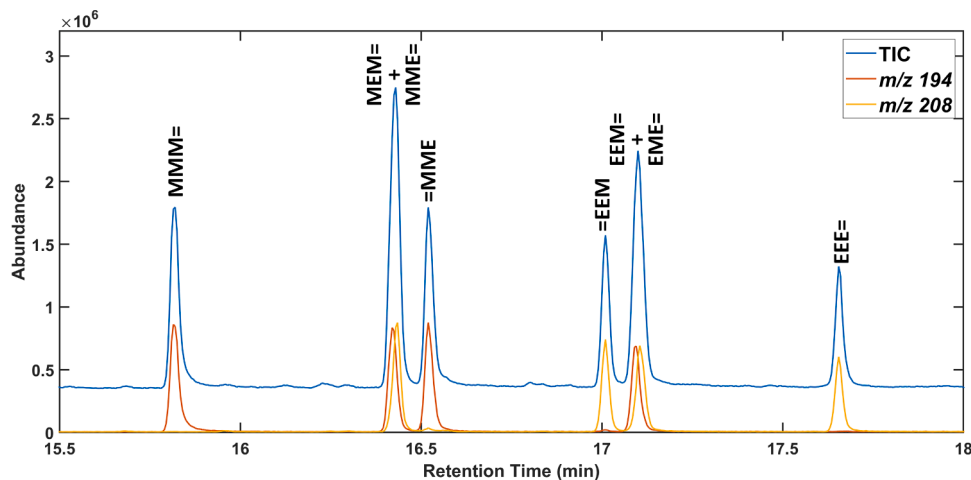


Fig. 4. Zoom in of the trimer region of a 54 % (mol/mol), MA-EA copolymer (Sample 3, Table 1) with assignment overlaid with the extracted ion chromatogram (EIC) of  $m/z$  194 and  $m/z$  208 both at 10x intensity. Here M and E refer to the MA and EA residues respectively, = indicates the location of the double bond.

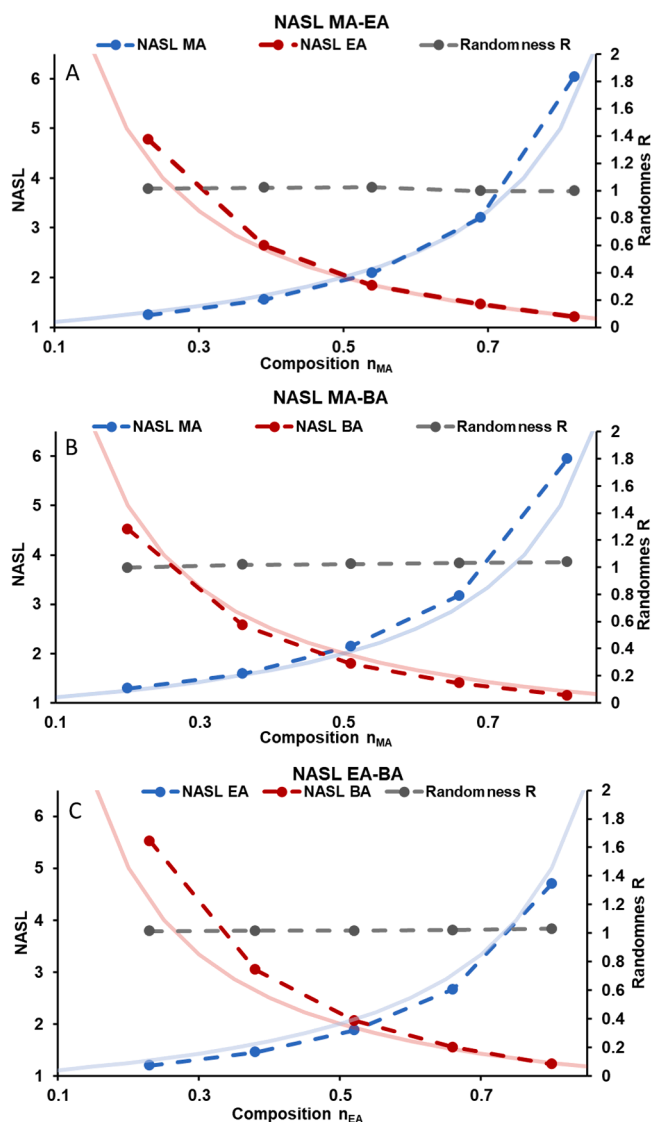


Fig. 5. Graphs featuring the determined NASL and randomness of the synthesized MA-EA (5 A), MA-BA (5B) and EA-BA (5 C) systems as determined by Py-GC-MS. The x-axis features the exact composition (molar fraction MA/EA) of the samples as determined by  $^1\text{H}$  NMR. The transparent lines indicate the theoretical sequence values for perfect Bernoullian copolymers.

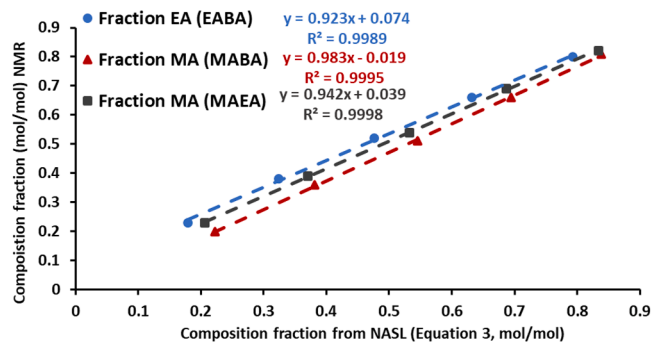


Fig. 6. Graph featuring the correlation between the determined composition with NMR and the composition as calculated based on the NASL as determined by Py-GC using Eq. 3.

### 3.2. Tertiary copolymers

Since the method functioned well for the sequence determination of binary copolymers, we aimed to expand it to tertiary systems. Ternary acrylate rubbers have been studied by Py-GC before using a micro-furnace pyrolyzer by Tsuge et al., yielding chromatograms with a similar structure, but have so far not been sequenced by Py-GC[16]. The synthesized tertiary (Table I sample 16–19) copolymers were therefore studied by Py-GC. The sequence of tertiary copolymers can be derived using similar equations incorporating the extra hybrid monomers as can be seen in Eq. 3 [24].

$$N_A = \frac{n_{AAA} + n_{AAB+BAA} + n_{AAC+CAA} + n_{BAB} + n_{CAC} + n_{BAC+CAB}}{\frac{1}{2}n_{AAB+BAA} + \frac{1}{2}n_{AAC+CAA} + n_{BAB} + n_{CAC} + n_{BAC+CAB}} \quad (3a)$$

$$N_B = \frac{n_{BBB} + n_{BBA+ABB} + n_{BBC+CBB} + n_{ABA} + n_{CBC} + n_{ABC+CBA}}{\frac{1}{2}n_{BBA+ABB} + \frac{1}{2}n_{BBC+CBB} + n_{ABA} + n_{CBC} + n_{ABC+CBA}} \quad (3b)$$

$$N_C = \frac{n_{CCC} + n_{CCA+ACC} + n_{CCB+BCC} + n_{ACA} + n_{BCB} + n_{ACB+BCA}}{\frac{1}{2}n_{CCA+ACC} + \frac{1}{2}n_{CCB+BCC} + n_{ACA} + n_{BCB} + n_{ACB+BCA}} \quad (3c)$$

A total of 27 signals must be assigned to sequence the tertiary copolymer, accounting for two forms of the various non-symmetrical trimers. While this might seem like a complicated task there is a clear structure to the pyrogram (Fig. 7, for a full chromatogram see Supplementary Fig. S6) easing assignment. There are clear clusters formed by the hybrid trimers which can be assigned based on comparison with the binary systems. Furthermore, since the separation is mainly based on volatility, the monomer composition can easily be correlated to retention times. The main challenge is in the assignment of the trimers containing three differing monomers. These trimers, the MBE, MEB and EMB trimers ( $t_R$  18.5–19 min), do not appear in the binary copolymers and can thus not be assigned by comparison of pyrograms. Instead, these polymers are assigned based on MS spectra and retention times. As demonstrated on the MA-EA systems the  $m/z$  194 and  $m/z$  208 are indicative of the double bond being present on a MA or EA monomer respectively. Furthermore, the  $m/z$  236 fragment is indicative of that on the BA monomer. Based on the trends observed in retention, where the monomer in the middle of the trimer contributes the least to retention, we would expect the following elution order: MBE then MEB and finally EMB. If we combine this with the information on the location of the double bond gained from MS we can come to a full assignment. Overall, we expect six peaks since the three monomers are asymmetrical and result in two peaks as the double bond can be on both ends. Thus, the first trimer signal in the ( $t_R$  18.5–19 min) cluster features a double bond on the EA monomer, based on the  $m/z$  208 signal, that combined with the early elution indicating BA to be the middle monomer, leads to the MBE= assignment. This signal is followed by two overlapping peaks with the double bond on MA and BA monomers, based the  $m/z$  194 and  $m/z$  236 signals respectively. Based on the early elution these signals can be assigned to =MBE and the next eluting species MEB=. The next peak features a double bond on a BA residue, partially by exclusion, this peak is assigned to the =BME. The final two overlapping signals feature a double bond on MA and EA can thus assigned to =MEB and BME=.

The assignment as shown in Fig. 7 was applied to calculate the NASL of four tertiary copolymer systems based on Eq. 3. The convoluted signals were deconvoluted by assuming equality of statistically identical peaks. The results of the sequence calculation can be seen in Fig. 8, the increase in NASL correlating to the increase in composition percentage can be clearly observed. The calculated randomness is constant across the samples.

While the actual degree of randomness of these tertiary copolymer systems is hard to verify, they are expected to be close to random due to the similar propagation rates [22]. To our knowledge, there is no published work on the sequencing of these complex acrylates systems by

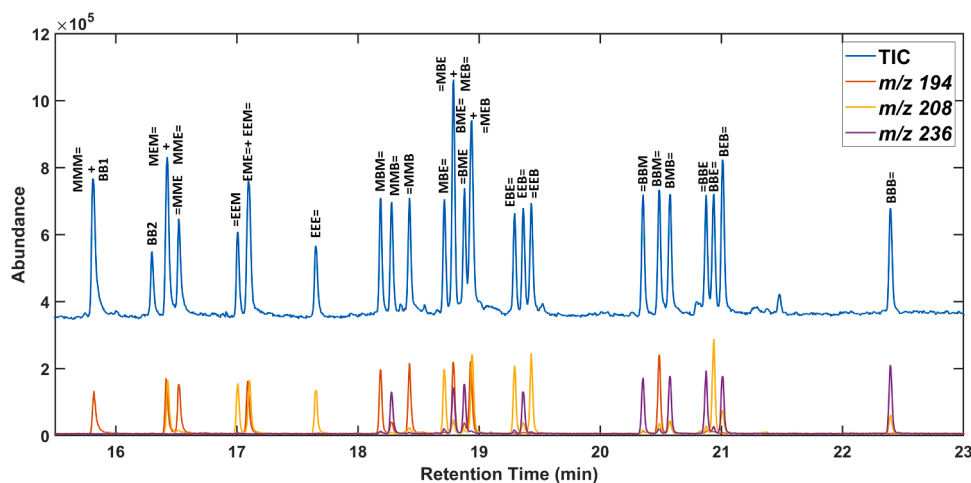


Fig. 7. Detailed view of the trimer region of MA-EA-BA tertiary copolymer (sample 16 Table 1). Here M, E and B refer to the MA, EA and BA residues respectively, = indicates the location of the double bond.

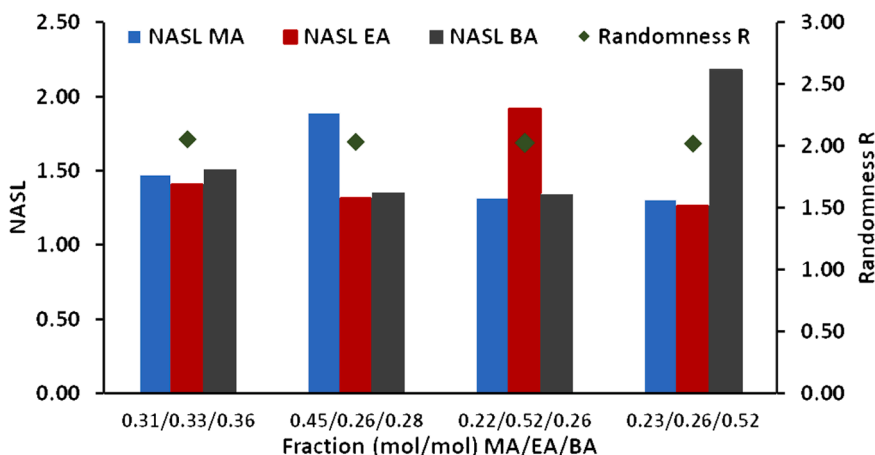


Fig. 8. Graph featuring the calculated NASL for four tertiary copolymer systems (samples 16–19 Table 1).

NMR. Doremaele et al. notes that they were unable to sequence a MA-BA copolymer due to tacticity effects dominating the spectra [7], which explains the lack of published NMR data on the sequence determination of acrylate systems. Another factor which should be considered is the recombination of monomers during pyrolysis, we studied this by pyrolyzing a blend of the three homopolymers (Supplementary Fig. S30). Minor recombination effects were observed, especially in the EA and MA monomers, this is unlikely to significantly affect the sequence determination of the systems studied in this work. It might influence the sequence determination of block and alternating copolymers more severely, however. We demonstrated that the sequence determination of acrylates by Py-GC based on the trimers signals is feasible. The trimers in the studied systems are typically baseline separated, the ones that are convoluted can easily be deconvoluted based on MS spectra, or pragmatically by assuming equality of statistically identical peaks (e.g. =AAB and BAA=). We managed to sequence various binary copolymers demonstrating that the overall randomness is close to one in all cases, which is to be expected for these copolymer systems. Since the various monomers applied in this study are chemically similar, little deviation in pyrolysis constants and MS response factors was observed. This might not be the case for all systems; therefore, we aim to further expand the method to systems featuring more chemically differing monomers, calibration with methods such as NMR might be required in those cases to obtain accurate sequence values.

#### 4. Conclusion

Insight in the sequence distribution of polymers is crucial for a deep insight in polymer properties. It is demonstrated that Py-GC can be used to determine the average sequence of acrylate copolymers. While previously applied to some copolymer systems, the Py-GC approach was expanded to more complex copolymer systems. The method was demonstrated on novel copolymer systems which are currently hard to sequence with NMR, the current standard in copolymer sequence determination. Furthermore, this is the first time that a tertiary (acrylate) copolymer is fully sequenced by Py-GC. This approach is a valuable tool to enhance the in-depth analysis of acrylate copolymers.

#### CRedit authorship contribution statement

**Wouter C. Knol:** Conceptualization, Methodology, Investigation, Visualization, Software, Formal analysis, Writing – original draft. **Sifra Vos:** Methodology, Investigation **Till Gruendling:** Supervision, Funding acquisition, Writing – review & editing. **Bob W.J. Pirok:** Conceptualization, Supervision, Writing – review & editing. **Ron A.H. Peters:** Conceptualization, Supervision, Funding acquisition, Project administration, Writing – review & editing.



## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2022.105578](https://doi.org/10.1016/j.jaap.2022.105578).

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