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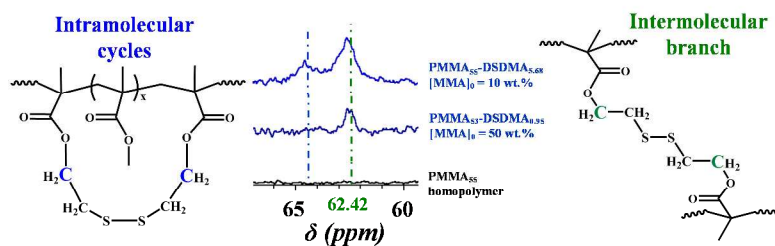
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Graphical Abstract:

Extent of intramolecular cyclization in RAFT-synthesized methacrylic branched copolymers using ^{13}C NMR spectroscopy

*J. Rosselgong and S. P. Armes**



**Extent of intramolecular cyclization in RAFT-synthesized methacrylic branched copolymers
using ^{13}C NMR spectroscopy**

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Abstract.

Recently, we reported using ^1H NMR spectroscopy to assess the degree of intramolecular cyclization in a series of soluble methacrylic branched copolymers (see J. Rosselgong and S. P. Armes, *Macromolecules*, **2012**, *45*, 2731-2737). The key to success in addressing this long-standing problem in polymer science was the selection of a suitable disulfide-based dimethacrylate as the branching comonomer, which was statistically copolymerized with methyl methacrylate using reversible addition-fragmentation chain transfer (RAFT) polymerization. In this earlier work, estimation of the degree of intramolecular cyclization required peak deconvolution of the relevant *thiamethylene* proton signals. In the present work, we show that quantitative ^{13}C NMR spectroscopy can also be utilized to determine the intramolecular cyclization for the same series of methacrylic copolymers via peak deconvolution of the *oxymethylene* carbon signals. Although this technique requires long spectral accumulation times, it offers superior resolution compared to ^1H NMR spectroscopy and hence may ultimately enable this analytical approach to be applied to less esoteric divinyl comonomers.

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Introduction

Over the past few decades, ^{13}C NMR spectroscopy has been demonstrated to be a versatile characterization tool in polymer science.¹⁻¹⁷ For example, the extent of long-chain branching has been assessed during the free radical solution polymerization of *n*-butyl acrylate, vinyl acetate or 2-ethylhexyl acrylate.^{2, 10, 14} Related studies conducted under emulsion polymerization conditions have implications for the grafting mechanism of polymeric stabilizers, which confer colloidal stability on the resulting latexes. More recently, this approach has been extended to include branching of *n*-butyl acrylate via living radical polymerization.^{15, 17} ^{13}C NMR has also been used to assess the oxidative degradation of polymers such as poly(ethylene oxide) and poly(propylene oxide).⁹ It has also proven to be a valuable tool for assessing monomer reactivity ratios¹⁴ and comonomer sequences,¹³ as well as assessing the extent of hydration of biomacromolecules¹² and micelle-forming block copolymers.^{15, 16} However, ^{13}C NMR spectroscopy is rather less convenient than ^1H NMR spectroscopy because the natural abundance of the former isotope is relatively low, which necessitates relatively long spectral accumulation times to ensure an acceptable signal-to-noise ratio. This problem is exacerbated if quantitative information is required, because delay times of up to twenty seconds are required between each spectrum to ensure that complete nuclear relaxation has occurred. Nevertheless, ^{13}C NMR remains attractive since it offers significantly higher spectral resolution than ^1H NMR. In principle, this is particularly useful when working with polymers, since their spectra are generally characterized by relatively broad signals.

Recently, we reported the use of ^1H NMR spectroscopy to assess the extent of intramolecular cyclization in soluble branched methacrylic copolymers prepared via reversible addition-fragmentation chain transfer (RAFT) polymerization according to the synthesis route shown in Figure 1.¹⁸ Although intramolecular cyclization had been studied both theoretically^{19, 20} and experimentally²¹ for various non-linear copolymer systems, our study provided the first spectroscopic evidence that this side reaction is favored when a monovinyl monomer is statistically copolymerized with a divinyl comonomer in *dilute* solution, whereas intermolecular branching is much more likely to occur when the same copolymerization is conducted in *concentrated* solution. In terms of the basic polymer physics, this is because intermolecular branching is unlikely to occur unless the growing polymer chains are above their critical overlap concentration, c^* .²² The key to tackling this long-standing problem in polymer science was the judicious selection of a suitable disulfide-based dimethacrylate branching comonomer (DSDMA, structure shown in Figure 1). The unusual dihedral angle of the S-S bond ensures that the two pairs of adjacent thiamethylene protons are relatively sensitive to their local environment. In addition, the choice of methyl methacrylate as the monovinyl monomer was also important since this minimized overlapping NMR signals in the spectral region of interest. When targeting one fully reacted DSDMA per copolymer chain, it was found that, only approximately half of these comonomer units actually produced intermolecular branching, with the remainder being 'wasted' in the form

of intramolecular cycles. Thus our data allowed the apparent conflict between classical gelation theory (which predicts that gelation should occur for just 0.50 fully-reacted divinyl comonomer units per primary chain)²³⁻²⁵ and many recent experimental studies (which indicate that at least one fully-reacted divinyl comonomer unit per primary chain is required for gelation)^{22, 26-35} to be finally resolved. However, even a conservative interpretation of the ¹H NMR spectra required peak deconvolution of complex spectral envelopes, which was only made possible by the fortuitous availability of appropriate model compounds in the literature.^{36, 37} In principle, this complex spectroscopic problem may be simplified by using ¹³C NMR spectroscopy rather than ¹H NMR spectroscopy, since the former technique offers much higher resolution. In the present work, we examine the use of ¹³C NMR spectroscopy to validate our earlier ¹H NMR study, with the ultimate aim of extending this spectroscopic approach to include other less esoteric divinyl branching comonomers.

Experimental

Branched copolymer syntheses

Detailed protocols for the synthesis of the various branched copolymers described in this manuscript have been recently reported elsewhere.^{22, 26}

¹³C NMR spectroscopy

All ¹³C NMR spectra were recorded at 125.75 MHz using a Bruker 500 MHz spectrometer at 328 K at a copolymer concentration of 200 mg.mL⁻¹ in CDCl₃ using a relaxation decay time of 20 s and averaged over 10,928 scans. ¹³C NMR spectra of the branched copolymers were analyzed using Topspin 2.1.6 software (Bruker Biospin). The relatively broad and complex ¹³C NMR signals corresponding to the two oxymethylene carbons (-O-CH₂-CH₂-S-S-: 62.42 ppm) due to the fully reacted DSDMA residues were deconvoluted using a Lorentzian fit. This involves fitting a Lorentzian function to each sub-peak within the spectral envelope so as to determine their respective areas, chemical shifts and widths (in ppm). This peak deconvolution protocol required three parameters: (i) the minimum intensity (*min int*) of the smallest sub-peak, (ii) the detection sensitivity (*det sens*) and (iii) the width overlap factor (*ov fac*) between adjacent sub-peaks. For the first iteration, these three parameters were always fixed as follows: *min int* = 0, *det sens* = 0.50, *ov fac* = 0.10. This routine typically generated a large number of sub-peaks with relatively weak intensities, most of which can be suppressed if the *min int* and the *det sens* parameters were then adjusted to obtain a more realistic (i.e. minimal) number of sub-peaks. For this Lorentzian line-shape fitting protocol, the oxymethylene carbons were observed at 62.42 ppm (with a peak-width of 0.05 ppm) in every case. A conservative approach was adopted for our peak deconvolution analysis: rather than attempting to assign the various individual intramolecular cycles, we simply focused on assessing the extent of intermolecular branching relative to the of intramolecular cyclization event (see Table 1). The experimental error incurred in determining the relative amount of intermolecular branching was estimated by systematically varying the *min int* parameter from zero up to a

value that afforded a reasonable number of sub-peaks (no more than ten) and an acceptable fit to the original spectrum. Intermolecular branching was attributed to a Lorentzian sub-peak centred at δ 62.42 ppm within the oxymethylene carbon spectral region.

Results and Discussion

Synthesis of soluble branched copolymers at various initial monomer concentrations

Recently, we reported the statistical copolymerization of methyl methacrylate (MMA) with varying amounts of the DSDMA branching comonomer using reversible addition-fragmentation chain transfer (RAFT) polymerization.^{22, 26} Three additional branched copolymers were prepared for the present study under the following conditions: (i) in the bulk (i.e. $[\text{MMA}]_0 = 100$ wt.%); (ii) at $[\text{MMA}]_0 = 75$ wt.% and (iii) at $[\text{MMA}]_0 = 10$ wt.%. The first and third of these copolymer samples had precisely the same targeted copolymer composition of $\text{PMMA}_{50}\text{-DSDMA}_{0.55}$. Given an estimated RAFT CTA efficiency of around 90%,²² this produced the actual branched copolymer compositions summarized in Table 1.

Quantitative assessment of the relative extents of intramolecular cyclization and intermolecular branching by peak deconvolution of ^{13}C NMR spectra

Compared to ^1H NMR spectroscopy, ^{13}C NMR spectroscopy offers potentially a more universal approach since its greater inter-peak resolution should enable extension to include other combinations of monovinyl monomers and divinyl branching agents.^{27-30, 32-35} In our original ^1H NMR study,¹⁸ our spectral assignments were considerably aided by the relatively simple copolymer spectra that resulted from the fortuitous combination of MMA monomer, DSDMA branching agent and CDB chain transfer agent, as well as the existence of nearly ideal cyclic model compounds available in the literature.^{36, 37} In the case of almost any other monovinyl methacrylic monomer, such ^1H NMR assignments would have been highly problematic due to the likelihood of overlapping signals arising from the monovinyl and divinyl comonomer residues. For example, the proton signals from, say, ethylene glycol dimethacrylate would be all but indistinguishable when copolymerized with, for example, ethyl methacrylate. However, the greater range of chemical shifts observed for ^{13}C NMR spectroscopy significantly reduces the probability of overlapping signals. However, this technique is limited by its inherently low sensitivity, since the natural abundance of the ^{13}C isotope is two orders of magnitude lower than that of the ^1H isotope. In principle, this problem can be overcome by accumulating a sufficiently large number of scans to enhance the spectral signal-to-noise, stipulating a sufficiently long relaxation time between each pulse and utilizing a high field spectrometer (see Experimental section for further details).

Unfortunately, no ^{13}C NMR spectra were reported by Hawker and co-workers for their cyclic disulfide monomer and corresponding copolymer, which proved to be highly convenient model compounds for our previous ^1H NMR spectroscopy studies.^{36, 37} Nevertheless, in their analysis of cross-linked copolymers, Borbély et al.¹³ stated that the oxymethylene signals of copolymerized ethylene glycol dimethacrylate units appear at 60 to 64 ppm. Figure 2 compares (i) linear PMMA₅₅ homopolymer prepared in the absence of any DSDMA comonomer and (ii) the series of PMMA₍₅₃₋₅₆₎-DSDMA_x copolymers prepared at $[\text{MMA}]_0 = 10, 30, 50, 75$ and 100 wt. % in the presence of increasing amounts of branching comonomer (*i.e.* 0.56, 0.68, 0.95, 1.70, 3.43 or 5.68 DSDMA units per primary chain). These DSDMA repeat units in the branched copolymer ^{13}C NMR spectra give rise to characteristic oxymethylene carbon signals in the 61-66 ppm region and thiamethylene carbon signals in the 35-40 ppm region. If it is assumed that the formation of intramolecular cycles affects the ^{13}C NMR chemical shift in the same way as the ^1H NMR chemical shift,¹⁸ *i.e.* that signals due to intramolecular cycles are shifted to higher ppm compared to the intermolecular branches, then the chemical shift due to the intramolecular cycles is at δ 62.42 ppm (for $-\text{O}-\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{S}-\text{S}-$) and δ 36.28 ppm (for $-\text{O}-\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{S}-\text{S}-$), as indicated by the dashed green lines shown in Figure 2.

Our original ^1H NMR assignments proved to be an invaluable starting point for the present work. For example, comparison of our ^1H NMR spectra with those of a cyclic disulfide monomer model compound and its corresponding copolymer prepared via ring-opening polymerization suggested that the DSDMA signals due to the intramolecular cycles should appear downfield relative to intermolecularly branched DSDMA repeat units. This hypothesis was confirmed after careful inspection of the ^1H NMR spectra recorded for eight PMMA-DSDMA branched copolymers prepared under various synthesis conditions (*i.e.* differing monomer concentrations and DSDMA/CTA molar ratios).

Further information that can be extracted by comparing these seven spectra is the presence of a sharp signal corresponding to the quaternary carbon of the CDB-derived end-group ($\text{Ph}-\text{CS}-\text{S}-\underline{\text{C}}(\text{CH}_3)_2-\text{Ph}$) at 37.81 ppm. This feature is well-separated from the thiamethylene carbon signals for the PMMA₅₃-DSDMA_{0.95} copolymer synthesized at 50 wt. %. However, for the copolymers prepared at 10 wt. %, which contain larger amounts of cycles, this quaternary carbon peak overlaps with the sub-peaks that correspond to the intramolecular cycles. In principle, the former signal can be used as an internal standard for quantifying the amount of DSDMA in the copolymer. In practice, the presence of this additional feature in the thiamethylene carbon region significantly complicates the peak deconvolution analysis.

Figure 3 shows the deconvoluted ^{13}C NMR spectra of the seven branched copolymers presented in Figure 2. Table 1 summarizes the extents of intramolecular cyclization estimated from peak deconvolution of the ^{13}C NMR spectra presented in Figure 3. All the sub-peaks that have not been identified as being due to intermolecular branching are assumed to be due to intramolecular cycles, without specifying the precise nature

of these cycles (i.e. the cycle size, whether primary or secondary cycles, etc.). The estimated experimental errors in each case correspond to the difference in peak areas obtained for the signal assigned to the intermolecularly-branched DSDMA units when conducting spectral deconvolutions using various fitting protocols.

Table 1 summarizes the final comonomer conversions ($> 95\%$ in all cases), molecular weights (M_w) and polydispersities (M_w/M_n) obtained for the seven methacrylic branched copolymers examined in this study. In each case the actual copolymer composition was close to that targeted, with minor discrepancies being attributed to incomplete comonomer conversions and imperfect CTA efficiency. It is instructive to compare entries 1 and 5 in Table 1. For these two syntheses, almost identical copolymer compositions of PMMA₅₅-DSDMA_{0.56} and PMMA₅₅-DSDMA_{0.59} were obtained, respectively. However, the former copolymer was prepared in the bulk, which produces a highly branched copolymer with an M_w of 115,300 and an M_w/M_n of 9.73; ^{13}C NMR analyses indicated a degree of intermolecular branching of $68 \pm 8\%$ in this case. In contrast, the latter copolymer prepared at 10 wt. % is only very lightly branched: GPC analysis indicated an M_w of 7,900 and an M_w/M_n of just 1.36, while the degree of intermolecular branching is estimated to be $31 \pm 9\%$. Thus in this case the majority of the copolymerized DSDMA repeat units are present as intramolecular cycles, rather than intermolecular branches. These striking differences illustrate the importance of the copolymer concentration in determining the structure of such branched copolymers. To a zeroth order approximation, the linear primary chains grow first (containing on average no more than one semi-reacted DSDMA comonomer). Thus significant branching only occurs towards the end of the reaction as the pendent vinyl group of the semi-reacted DSDMA comonomer begins to participate in the copolymerization. Whether this leads to intermolecular branching or intramolecular cyclization depends on whether the growing copolymer chains are above or below their critical overlap concentration (c^*). For primary chains with a mean degree of polymerization of 55, c^* has been calculated to be approximately 14.6 wt. %.²² Hence this conceptual framework is fully consistent with the experimental observations and moreover explains why no macroscopic gelation is observed even when targeting either three or five DSDMA comonomer units per primary copolymer chain (see entries 6 and 7 in Table 1). In these latter two cases, 92-93% of the DSDMA comonomer units participate in intramolecular cyclization, rather than intermolecular branching. It is also noted that, for entry 4 in Table 1, ^{13}C NMR analysis affords a very similar result to that obtained by ^1H NMR spectroscopy. In the case of this highly branched PMMA₅₆-DSDMA_{1.70} copolymer ($M_w = 358\,700$; $M_w/M_n = 22.17$), there are approximately 0.59 intermolecular branches per primary copolymer chain as judged by ^{13}C NMR studies, which is close to the 0.61 value calculated by ^1H NMR spectroscopy, as reported earlier.¹⁸

Overall, ^{13}C NMR and ^1H NMR analyses yield similar degrees of intermolecular branching, see Table 1. In particular, the additional two branched copolymer prepared at $[\text{M}]_0 = 75\text{ wt.}\%$ and $100\text{ wt.}\%$ conform to the anticipated general trend: the extent of intramolecular cyclization is significantly reduced for syntheses conducted at higher copolymer concentrations (see penultimate column in Table 1). This is because

interpenetration of the growing copolymer chains is much more likely under these conditions, which is a pre-requisite for efficient intermolecular branching.¹⁸ However, there is an apparent discrepancy for the highly branched PMMA₅₃-DSDMA_{0.95} copolymer prepared at 50 wt.% (see entry 3 in Table 1). This copolymer exhibits a degree of intermolecular branching of 46 ± 7 % as judged by ¹³C NMR spectroscopy but 61 ± 7 according to ¹H NMR spectroscopy. The reason for this apparent discrepancy is not known, but it is noted that the difference is close to being within the estimated experimental errors.

Finally, the quaternary carbon assigned to the CDB-derived RAFT chain-end adversely affects spectral deconvolution of the thiamethylene region. This is illustrated for the branched copolymer prepared at 50 wt. % (see entry 3 in Table 1). In contrast, peak deconvolution of the oxymethylene carbon signals is relatively straightforward and reproducible. Thus the latter spectral region is preferred for calculation of the mean degree of intermolecular branching, with the degree of intramolecular cyclization being determined by difference. The latter values are similar to those obtained from the ¹H NMR spectra, at least within experimental error (see final column in Table 1). However, because of its very low abundance, ¹³C NMR has a relatively poor signal-to-noise ratio compared to ¹H NMR, especially for the two spectral regions of interest. With the benefit of hindsight, it is clear that if an *aliphatic* RAFT CTA had been used to prepare these branched copolymers (rather than the aromatic CDB), it should be possible to analyze the thiamethylene carbon signals, in addition to the oxymethylene spectral region.

Conclusions

¹³C NMR spectroscopy can be used to determine the degree of intramolecular cyclization in soluble branched methacrylic copolymers. In the specific case of a disulfide-based dimethacrylate branching agent, the oxymethylene carbon atoms are more amenable to analysis than the thiamethylene carbon atoms. In contrast, when using ¹H NMR spectroscopy it was found that the thiamethylene proton signal was more information-rich than the oxymethylene proton signal. Generally speaking, these two spectroscopic techniques indicate similar degrees of intermolecular branching, see Table 1. In particular, the additional two branched copolymer prepared at [M]₀ = 75 wt.% and 100 wt.% follow the anticipated general trend: the extent of intramolecular cyclization is significantly reduced for syntheses conducted at higher copolymer concentrations (see penultimate column in Table 1). This is because interpenetration of the growing copolymer chains is much more likely under these conditions, which is a pre-requisite for efficient intermolecular branching.¹⁸ Finally, it is emphasized that, although ¹³C NMR spectroscopy requires relatively long accumulation times, its higher resolution may offer some advantages compared to ¹H NMR spectroscopy, particularly when attempting to generalize this method to include less esoteric branching comonomers.

Acknowledgments.

Mrs S. Bradshaw and Dr. B. Taylor are thanked for performing the ^{13}C NMR experiments. EPSRC is acknowledged for funding this work (Platform Grant EP/J007846/1). This material is available free of charge via the Internet at <http://pubs.acs.org>. This study is dedicated to the memory of Marie-Dominique Rosselgong Saint-Amans.

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Figures

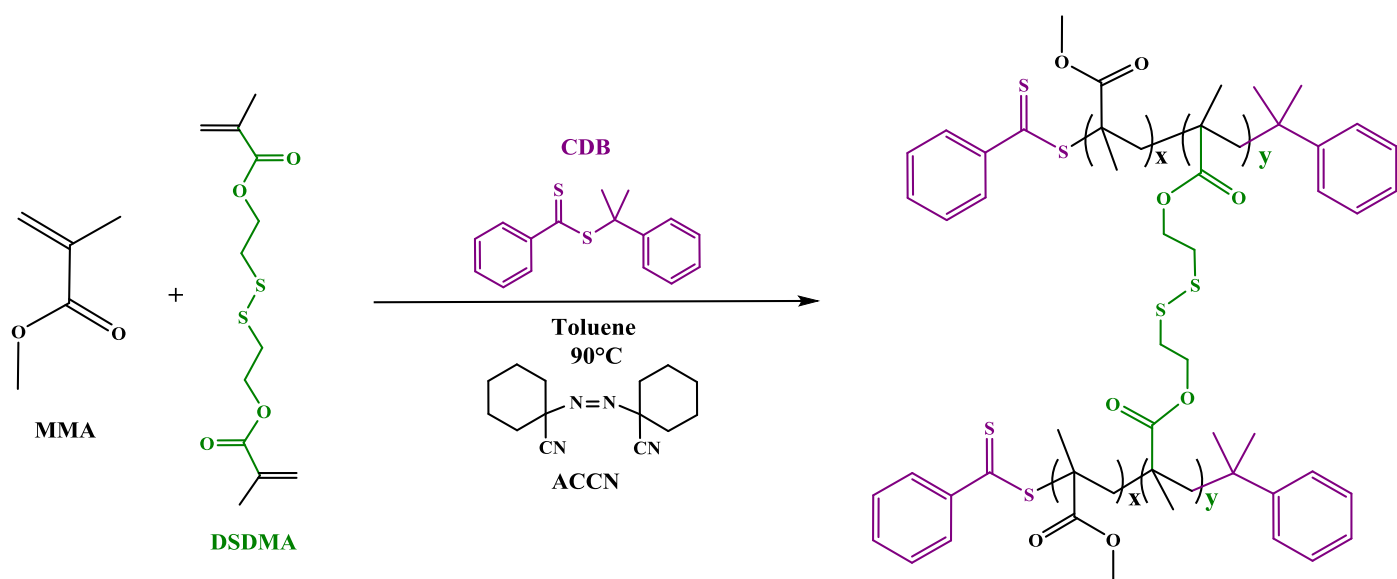


Figure 1. Synthesis of the methacrylic branched copolymers prepared using reversible addition-fragmentation chain transfer (RAFT) polymerization. Statistical copolymerization of methyl methacrylate (MMA) with varying amounts of a disulfide-based dimethacrylate (DSDMA) branching comonomer was achieved using a cumyl dithiobenzoate (CDB) chain transfer agent and 1,1'-azobiscyclohexanecarbonitrile (ACCN) initiator in toluene at 90°C.

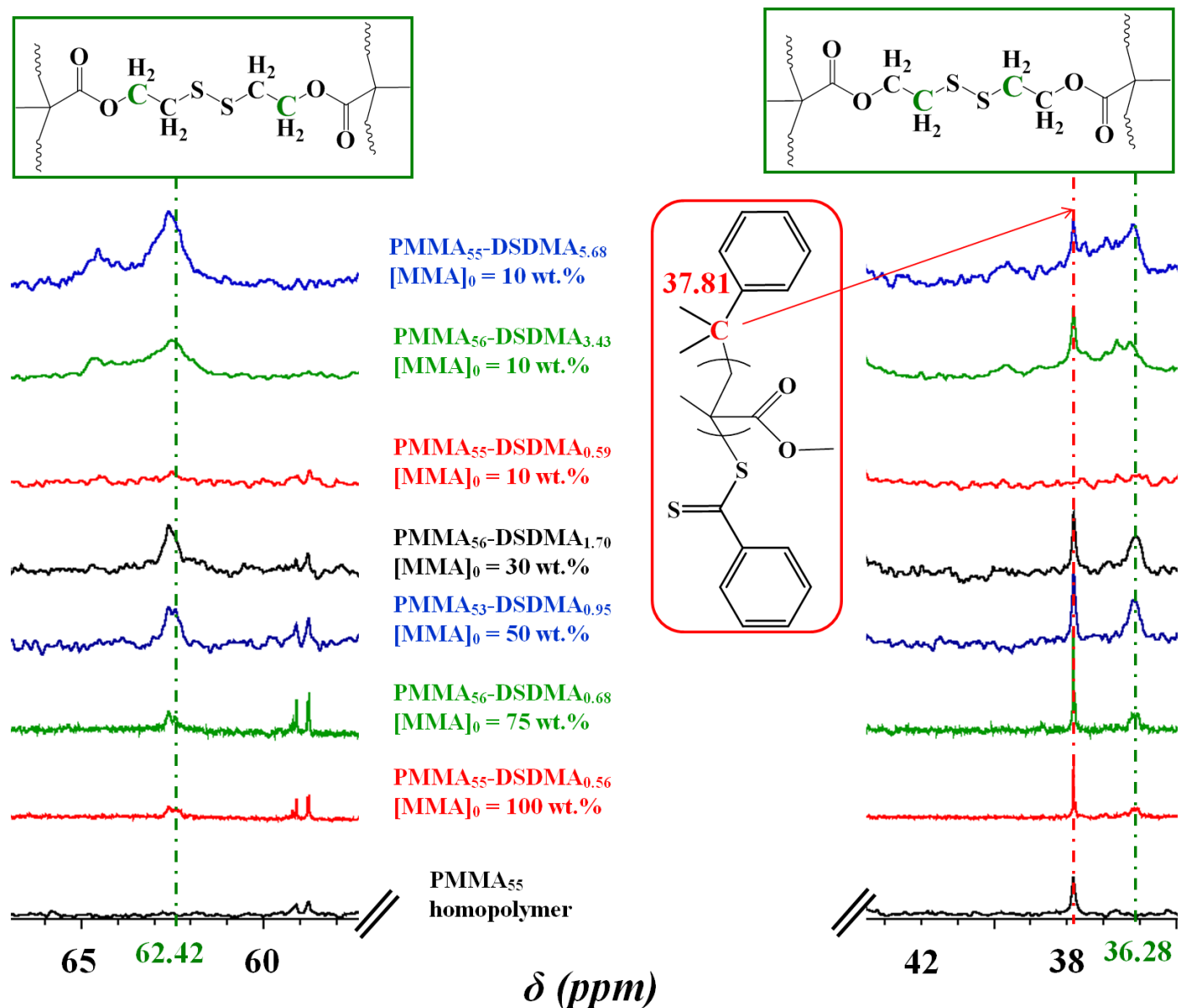


Figure 2. Oxymethylene and thiamethylene regions of the ^{13}C NMR spectra (recorded in CDCl_3 at 25°C) for soluble $\text{PMMA}_{(53-56)}\text{-DSDMA}_x$, branched copolymers prepared at $[\text{MMA}]_0 = 100$ wt. %, 75 wt. %, 50 wt. %, 30 wt. % and 10 wt. % via RAFT statistical copolymerization of MMA with DSDMA with CDB as chain transfer agent and ACCN initiator in toluene at 90°C .

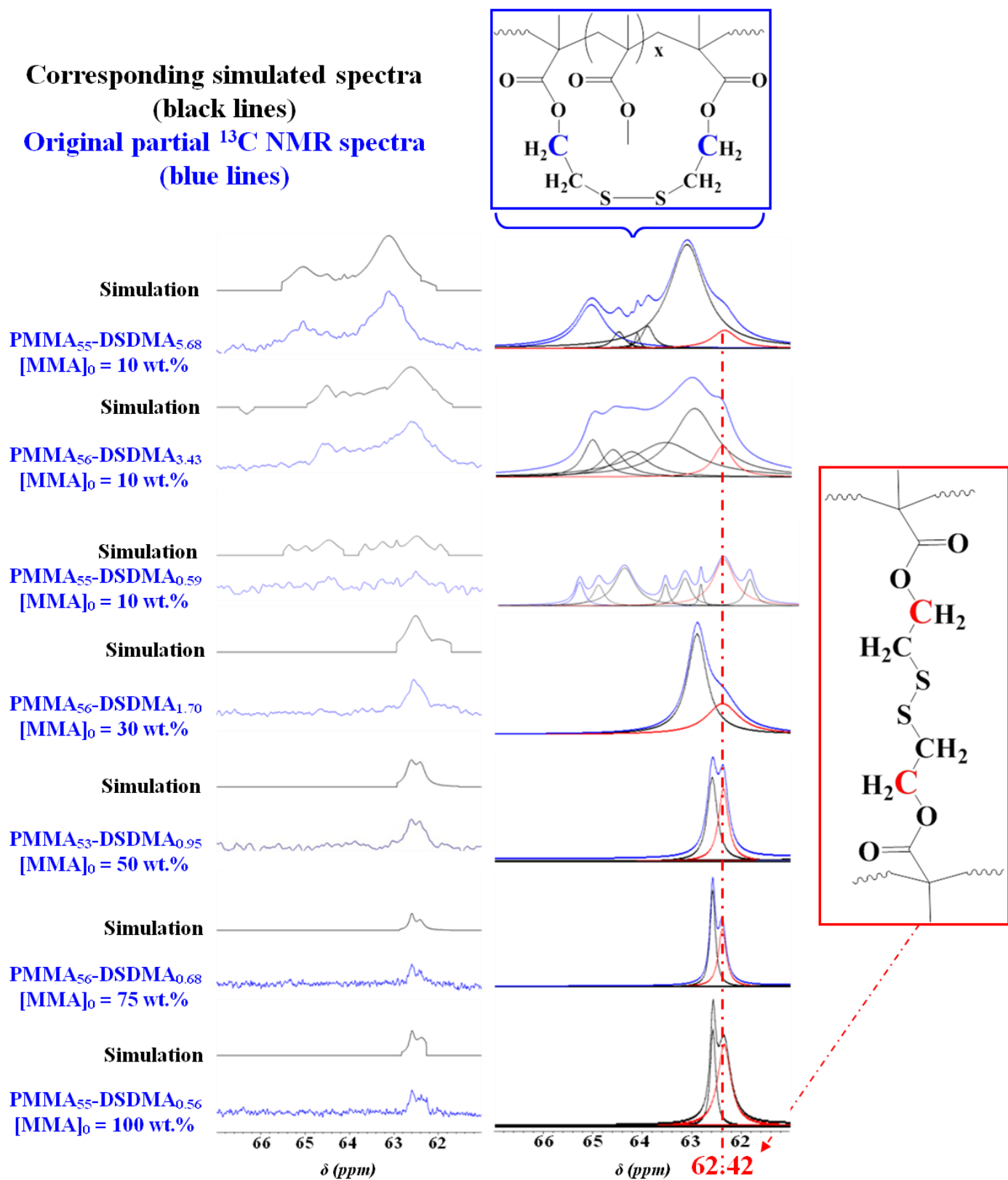


Figure 3. Oxymethylene region of the deconvoluted ^{13}C NMR spectra (recorded in CDCl_3 at 25°C) for soluble $\text{PMMA}_{(53-56)}\text{-DSDMA}_x$, branched copolymers prepared at $[\text{MMA}]_0 = 100$ wt. %, 75 wt. %, 50 wt. %, 30 wt. % and 10 wt. % via RAFT statistical copolymerization of MMA with DSDMA with CDB as chain transfer agent and ACCN initiator in toluene at 90°C .

List of Tables

Table 1. Summary of branched copolymer compositions (*targeted composition, **calculated by end-group ^1H NMR analysis; soluble fraction), final comonomer conversion for a series of soluble branched copolymers prepared by RAFT at various initial comonomer concentrations using increasing amounts of DSDMA branching comonomer. Molecular weight data were obtained by DMF GPC using a refractive index detector (calibrated using a series of narrow dispersed poly(methyl methacrylate) standards). The relative degrees of intramolecular cyclization and intermolecular branching (and estimated associated experimental errors) were calculated for various soluble branched copolymers via peak deconvolution of their ^{13}C NMR spectra.

$[\text{M}]_0^{\text{a}}$ (wt.%)	Targeted copolymer composition**	Calculated copolymer composition**	Conv. (%)	M_w (g mol^{-1})	M_w/M_n	Inter ^{13}C (%)	Intra ^{13}C (%)	Inter $^1\text{H}^{\text{b}}$ (%)
100	PMMA ₅₀ -DSDMA _{0.55}	PMMA ₅₅ -DSDMA _{0.56}	98.2	115,300	9.73	68 ± 8	32 ± 8	N/D
75	PMMA ₅₀ -DSDMA _{0.65}	PMMA ₅₆ -DSDMA _{0.68}	97.6	55,700	4.70	47 ± 6	53 ± 6	N/D
50	PMMA ₅₀ -DSDMA _{0.90}	PMMA ₅₃ -DSDMA _{0.95}	96.6	233,100	14.49	46 ± 7	54 ± 7	61 ± 7
30	PMMA ₅₀ -DSDMA _{1.50}	PMMA ₅₆ -DSDMA _{1.70}	98.7	358,700	22.17	35 ± 8	65 ± 8	36 ± 6
10	PMMA ₅₀ -DSDMA _{0.55}	PMMA ₅₅ -DSDMA _{0.59}	95.8	7,900	1.36	31 ± 9	69 ± 9	N/D
10	PMMA ₅₀ -DSDMA _{3.00}	PMMA ₅₆ -DSDMA _{3.43}	96.1	27,500	2.51	8 ± 7	92 ± 7	8 ± 2
10	PMMA ₅₀ -DSDMA _{5.00}	PMMA ₅₅ -DSDMA _{5.68}	96.4	138,200	7.71	7 ± 6	93 ± 6	10 ± 5

a. $([\text{M}]_0 = ([\text{DSDMA}]_0 + [\text{MMA}]_0)/[\text{m}_{\text{solvent}} + [\text{DSDMA}]_0 + [\text{MMA}]_0])$

b. Extent of intermolecular branching determined from ^1H NMR analysis.¹⁸