

# Olefin copolymerization *via* reversible addition–fragmentation chain transfer†

Rajan Venkatesh, Bastiaan B P Staal and Bert Klumperman\*

Dutch Polymer Institute, Eindhoven University of Technology, Department of Polymer Chemistry, Den Dolech 2, P O Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: L. Klumperman@tue.nl; Fax: +31-40-2463966; Tel: +31-40-2472339

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**Successful statistical copolymerization of an  $\alpha$ -olefin (1-octene) with an acrylate (butyl acrylate, BA) and with a methacrylate (methyl methacrylate, MMA), employing reversible addition–fragmentation chain transfer (RAFT) mediated polymerization has been accomplished**

Copolymers of  $\alpha$ -olefins with polar monomers with various architectures are of great relevance to polymer science. The incorporation of polar groups into a quite non-polar material will lead to substantial changes in its physical properties.<sup>1</sup> It is known that  $\alpha$ -olefins cannot be homopolymerized *via* a free radical mechanism. This is attributed to the fact that  $\alpha$ -olefins undergo degradative chain transfer of allylic hydrogens.<sup>2</sup> The stable allylic radical derived from the monomer is slow to reinitiate and prone to terminate. On the other hand, polar vinyl monomers polymerize readily *via* a free radical mechanism. Copolymerization of methyl acrylate and  $\alpha$ -olefin has been reported using metal-catalyzed insertion mechanism.<sup>3</sup> Catalyst systems showing excellent behavior for both olefins and polar monomers exist. However, true (statistical) copolymerization of these two types of monomer is difficult to achieve due to the very unfavorable reactivity ratios in conjunction with these catalyst systems. Recent developments were indicative of the fact that  $\alpha$ -olefins may be copolymerized with vinyl monomers *via* a free radical technique.<sup>4</sup> However, polymers with broad molar mass distributions (MMDs) were obtained, as a result of chain transfer and termination events, which normally occur during free radical polymerization. The only other documented example has been the copolymerization of methyl acrylate and methyl methacrylate with  $\alpha$ -olefins using a copper-mediated polymerization technique.<sup>5,6</sup>

The present paper reports, the statistical copolymerizations of an acrylate (butyl acrylate, BA) and methacrylate (methyl methacrylate) with an  $\alpha$ -olefin (1-octene), using reversible addition–fragmentation chain transfer (RAFT) mediated polymerization.<sup>7–10</sup> Well controlled RAFT homopolymerization of PBA and PMMA have been reported using the employed RAFT agents.<sup>11–13</sup> However, the copolymerization reactions are highly unlikely due to MMA's low homopropagation rate coefficient ( $k_p$ ), coupled with the fact that  $\alpha$ -olefins undergo degradative chain transfer reactions as previously explained. Further, to initiate the RAFT reactions, normal free radical thermal initiators (like  $\alpha, \alpha'$ -azobisisobutyronitrile, AIBN) are employed, hence there was a large probability that the copolymerization if occurring, may not be controlled, since as previously stated, chain transfer and termination events dominate during free radical polymerization. But, in spite of the challenges posed, copolymers of the polar monomers with 1-octene with narrow MMD were obtained. Another advantage, which the RAFT technique offers, is that the polymer can be used directly without any cumbersome purification steps.

Conventional free radical copolymerization and RAFT copolymerization of BA and 1-octene (Oct) were examined as summarized in Table 1. Table 2 shows the results for the MMA and 1-octene copolymers.

From the data in Table 1 and 2, the following observations can be made; (i) A significant fraction of 1-octene was incorporated during the RAFT experiments. (ii) Narrow MMDs were obtained for the RAFT reactions, which implied that no peculiarities were caused by the incorporation of the 1-octene. (iii) The linear increase of  $M_n$  as a function of monomer conversion is indicative of the living character of the RAFT polymerization [see Supplementary Information†]. (iv) When the mol% of the olefin was increased in the monomer feed, its incorporation was higher in the copolymer, but the overall conversion decreased. (v) Comparable FRP reactions, resulted in polymers with broad MMDs.

The incorporation of both monomers in a statistical copolymer was shown using matrix assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS) and <sup>13</sup>C NMR spectroscopy. Reverse phase gradient polymer elution chromatography (GPEC) with water and acetonitrile as eluent was employed for selective separation based on chemical composition.

Fig. 1 is an expansion of a selected portion from the MALDI-TOF-MS spectrum obtained for BA/1-octene copolymer (Table 1, entry 2). The whole spectrum is shown in the supplementary information†. The polymer chains were all cationized with sodium.

**Table 1** Copolymers of BA/1-octene

Entry	$f_{\text{Oct}}$	Overall Conv. <sup>d</sup>	$F_{\text{Oct}}$ <sup>d</sup>	$M_n$ (g mol <sup>-1</sup> )	PDI
1* <sup>a</sup>	0.25	0.70	0.08	$2.8 \times 10^3$	1.3
2* <sup>b</sup>	0.50	0.53	0.22	$2.4 \times 10^3$	1.3
3# <sup>c</sup>	0.25	0.73	0.07	$6.6 \times 10^3$	2.9
4# <sup>c</sup>	0.50	0.52	0.16	$5.2 \times 10^3$	2.4

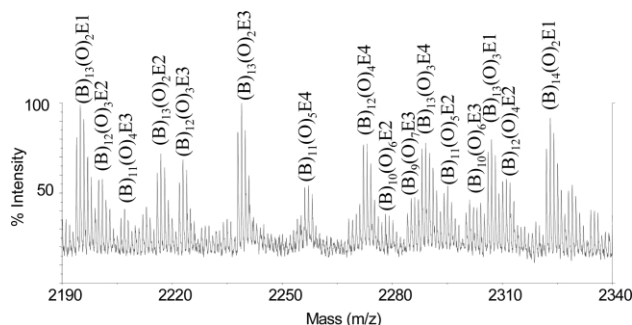
\* RAFT reactions. # Free radical polymerization (FRP). Solvents for the copolymerizations – Mixture of methyl ethyl ketone (MEK) and *p*-xylene in 1 : 1 volume ratio. Volume of {monomer}/solvent = 0.25/1. Reaction temperature = 80 °C. RAFT copolymerizations – [Monomer] : [S,S'-Bis( $\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid)trithiocarbonate]<sup>11</sup> : [AIBN] = 36.8 : 1 : 0.18.<sup>a</sup> Reaction time = 10 h. <sup>b</sup> Reaction time = 11 h 30 min. FRP copolymerizations –  $\alpha, \alpha'$ -azobisisobutyronitrile, AIBN (10 mmol L<sup>-1</sup>). <sup>c</sup> Reaction time = 11 h. <sup>d</sup> Calculated from values, obtained from gas chromatography (GC) measurements.

**Table 2** Copolymers of MMA/1-octene

Entry	$f_{\text{Oct}}$	Overall Conv. <sup>a</sup>	$F_{\text{Oct}}$ <sup>a</sup>	$M_n$ (g mol <sup>-1</sup> )	PDI
1*	0.25	0.55	0.09	$2.9 \times 10^3$	1.3
2*	0.50	0.44	0.20	$1.7 \times 10^3$	1.3
3#	0.25	0.73	0.06	$1.8 \times 10^4$	3.1
4#	0.50	0.58	0.16	$1.0 \times 10^4$	4.2

\* RAFT reactions. # – Free radical polymerization (FRP). Solvent for the copolymerizations – *p*-xylene. RAFT copolymerizations – [Monomer] : [2-cyanopropyl-2-yl dithiobenzoate] : [V-65, 2,2'-azobis(2,4-dimethylvaleronitrile)] = 47.6 : 1 : 0.125. Volume of {monomer}/solvent = 1/0.5. Reaction temperature = 50 °C. Reaction time = 20 h. FRP copolymerizations –  $\alpha, \alpha'$ -azobisisobutyronitrile, AIBN (10 mmol L<sup>-1</sup>). Volume of {monomer}/solvent = 0.5/1. Reaction temperature = 90 °C. Reaction time = 25 h.<sup>a</sup> Calculated from values, obtained from gas chromatography (GC) measurements.

† Electronic supplementary information (ESI) available: experimental details, <sup>13</sup>C NMR, MALDI-TOF-MS spectra of copolymers and kinetic plots. See <http://www.rsc.org/suppdata/cc/b4/b403342f>

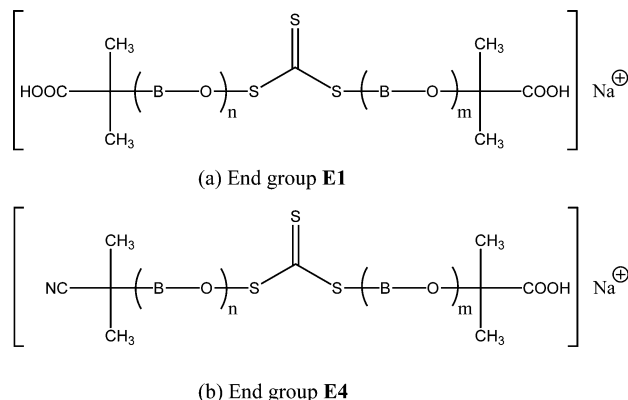


**Fig. 1** Expansion of a selected portion from the MALDI-TOF-MS spectrum of P[(BA)-co-(octene)] copolymer.  $f_{\text{octene}} = 0.50$ ,  $F_{\text{octene}} = 0.22$ . Spectrum acquired in reflector mode; matrix – DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile). The complete spectrum is shown in the supplementary information†.

All the polymer chains were assigned to various chemical compositions, constituting of varying BA (B) and 1-octene (O) units. All copolymer chains can be divided into having four pairs of end groups.

During the RAFT copolymerization, the polymeric chains can propagate in both directions, since, *S,S'*-bis( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid)trithiocarbonate is a bifunctional RAFT agent, resulting in end group **E1** as shown in Fig. 2(a). The end group pairs **E2** and **E3** originated as a result of the exchange reaction between the proton of the COOH group and a sodium cation during MALDI-TOF-MS analysis. In the case of end group pair **E2** only one proton is exchanged for the sodium, and for end group pair **E3** both protons are exchanged. Hence, for copolymer chains having identical chemical composition, the copolymer chains with end groups **E2** and **E3** are detected at higher masses differing by 22 Daltons and 44 Daltons respectively, as compared to chains having **E1** as the end group. The initiator AIBN is added at predetermined time intervals during the copolymerization so as to generate radicals and keep the RAFT polymerization process active. Hence, some chains can be initiated by the primary cyanoisopropyl radical. The structure for end group pair **E4** represents a case wherein one of the end groups is the AIBN fragment [Fig. 2(b)]. As summarized in Table 3 it is evident from the MALDI-TOF-MS spectrum (shown in Fig. 1) that several units of 1-octene were incorporated within the polymer chain.

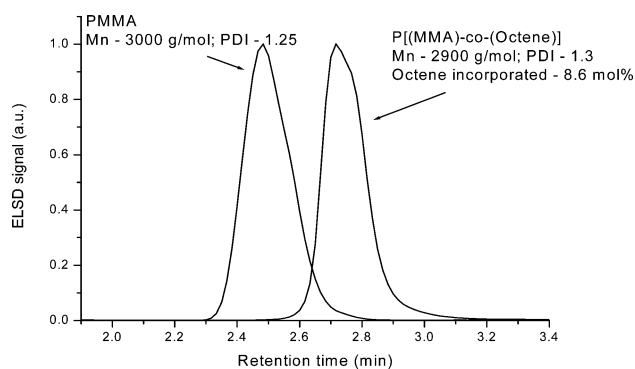
In the  $^{13}\text{C}$  NMR spectrum for BA/1-octene copolymer, two signals were observed in the carbonyl region ( $\delta$  174.5 and 175.9 ppm).† The peak at  $\delta$  174.5 ppm, is assigned to the carbonyl carbon present in long BA runs. The peak at  $\delta$  175.9 ppm is assigned to a BA carbonyl adjacent to an octene. The current assignments are based on a publication wherein a  $^{13}\text{C}$  NMR spectrum of methyl acrylate/ $\alpha$ -olefin is assigned.<sup>4</sup> The presence of this peak also



**Fig. 2** The end group pairs **E1** and **E4** observed during MALDI-TOF-MS analysis of the BA/octene copolymers. B and O are the abbreviations for butyl acrylate and 1-octene respectively.

**Table 3** Peak assignments for the MALDI-TOF-MS spectrum of P[(BA)-co-(octene)] copolymer in Fig. 1 ( $f_{\text{octene}} = 0.50$ ,  $F_{\text{octene}} = 0.22$ )

Peak	BA units	Octene units	Observed mass (Da)	Theoretical mass (Da)	$\text{Na}^+$
$\text{B}_{13}\text{O}_2\text{E1}$	13	2	2195.0061	2195.3369	1
$\text{B}_{13}\text{O}_2\text{E2}$	13	2	2216.9749	2217.3188	2
$\text{B}_{13}\text{O}_2\text{E3}$	13	2	2238.9600	2239.3008	3
$\text{B}_{11}\text{O}_5\text{E4}$	11	5	2257.1845	2257.2921	1



**Fig. 3** GPEC traces of PMMA and of P[(MMA)-co-(octene)]. Eluent – water/acetonitrile (40/60 to 0/100 in 20 mins). CN-modified Si-column.

provides further evidence that the octene is incorporated into the same polymer chains as BA.

The GPEC trace in Fig. 3 clearly indicates well-resolved peaks from the homopolymer of MMA and the copolymer of MMA and 1-octene, wherein 8.6 mol% of octene was incorporated. The difference in the elution behavior was a direct indication of chemical composition difference between the homopolymer and the copolymer.

In conclusion, the RAFT copolymerization of acrylate and methacrylate with 1-octene results in real copolymers with narrow MMD and significant incorporation of the olefin in the polymer chain.

## Notes and references

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