Reversible addition-fragmentation chain transfer (RAFT) polymerization of alkyl-2-cyanoacrylates: An assessment of livingness

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ABSTRACT

Alkyl 2-cyanoacrylates (CAs) are primarily used as instant adhesives, including those sold under the Loctite brand. The adhesive action can be inhibited with acid stabilizers allowing radical polymerization to be employed. The following article details the first attempted controlled/living radical polymerization of alkyl CAs: Reversible addition fragmentation chain transfer (RAFT) polymerization mediated by a poly(methyl methacrylate) dithiobenzoate macroRAFT agent for three different CA monomers (ethyl 2-cyanoacrylate, *n*-butyl 2-cyanoacrylate and 2-phenylethyl cyanoacrylate) allowed the preparation of the first block copolymers of this challenging but commercially important monomer class. Nevertheless, GPC with UV detection indicated significant loss of the RAFT end-group for all three CAs limiting control/living character.

KEYWORDS: Instant Adhesives, controlled/living polymerization, block copolymer, macroRAFT

INTRODUCTION

Alkyl 2-cyanoacrylates (alkyl CAs, Fig. 1) are a monomer class best known as major components of industrial and household instant adhesives or super glues, including those sold commercially under the Loctite brand.[1-3] Once applied to a surface, moisture initiates the liquid alkyl CA monomer to cure within seconds due to rapid anionic polymerization.[4,5] Smaller CAs such as ethyl 2-cyanoacrylate (ECA) provide powerful instantaneous bonding between a wide variety of surfaces, including ceramics, plastics, and metals, whereas CAs with longer R-groups such as *n*-butyl 2-cyanoacrylate (*n*BCA) have greater biocompatibility, and have found use in wound closure, dentistry and medicine.[2,6,7] 2-Phenylethyl cyanoacrylate (PECA) differs from the previously named two CAs in that it is a solid and is utilised in industrial adhesive tapes and films.[8,9]
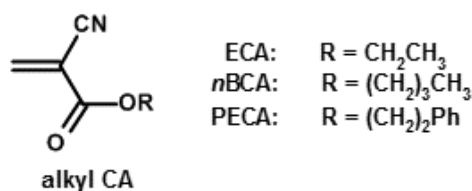
FIGURE 1 Alkyl 2-cyanoacrylates (alkyl CAs).

Under acidic conditions, which inhibit the facile anionic pathway,[10] CAs can be polymerized radically, with the propagation rate coefficient (k_p) reported as 1610 L·mol^{-1}·s^{-1} at 30 ^{o}C for ECA using the rotating sector method by Yamada et al.[11] Recently the k_p for nBCA was reported as 226 ± 32 L·mol^{-1}·s^{-1} at 30 ^{o}C using the more accurate pulsed-laser polymerization coupled with size exclusion chromatography (PLP-SEC) technique.[12] Conventional (non-living) radical copolymerization of ECA with methyl methacrylate (MMA) has been reported to result in random copolymers with an alternating tendency,[12,13] and having greater thermal stability than poly(ECA) homopolymers.[13] There are however no reported attempted controlled/living radical polymerizations (CLRP) of the CA monomer family. Reversible addition-fragmentation chain transfer (RAFT) polymerization is perhaps the most versatile CLRP technique in terms of tolerance to monomer functionality and reaction conditions.[14,15] Other established techniques such as atom transfer radical polymerization (ATRP)[16] and nitroxide-mediated polymerization (NMP)[17] are deemed unsuitable for CAs because of the basicity of reactants, for example the amine ligands commonly used in ATRP and the alkoxyamine functional group in NMP would initiate unwanted anionic polymerizations.

The present paper deals with RAFT polymerization of various CA monomers. It is demonstrated that diblock and triblock copolymers can be prepared with some success, although the control/livingness is hampered by RAFT end group loss. It is proposed that RAFT end group decomposition followed by a cascade of side reactions results in a complex reaction system with compromised control/livingness.

EXPERIMENTAL

<u>Materials</u>

Methyl methacrylate (MMA) (99%, Aldrich) was used after removal of monomethyl ether hydroquinone (MEHQ) radical stabilizer by passing through columns pre-packed with inhibitor removers (Aldrich). Anhydrous toluene (99.8%, Alfa Aesar), cyanoisopropyl dithiobenzoate (CPDB) (>97%, Strem Chemicals Inc.), 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid (CDSPA) (>97%, Aldrich), 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTPA) (>97%, Aldrich), 1,3-propanesultone (98%, Aldrich) and methanesulfonic acid (MSA) (≥99.5%, Aldrich) were all used as received. Methyl (ethoxycarbonothioyl)sulfanyl acetate (MESA) was prepared as previously described.[18] Ethyl cyanoacrylate (ECA, 99%), n-butyl cyanoacrylate (nBCA, 98%) and phenylethyl cyanoacrylate (PECA, 99%) were received from Henkel Ireland, and vacuum distilled prior to use to remove inhibitors. Azo(isobutyronitrile) (AIBN) (97%, VWR Ireland) and 1,1'-azobis(cyclohexanenitrile) (ACN) (98%, Aldrich) were recrystallized from methanol and dried under vacuum. Polymerization solutions were purged with nitrogen and immersed in an oil bath at the required temperature for the prescribed time, and quenched by placing the opened reactions on an ice bath. Viscous polymerization mixes were dissolved in a minimum of acetone prior to precipitation by dropwise addition into tenfold excess of cold methanol containing 0.05% $^w/_v$ MSA for CA polymerizations (and without MSA for macroRAFT and triblock polymerizations). Viscous polymerization mixes were dissolved in a minimum of acetone prior to precipitation. After purification polymers were dried under vacuum to a constant weight, and conversions were measured gravimetrically.

Instrumentation and Measurements

Molecular weight distributions were recorded using size exclusion chromatography (SEC) at 30 $^{\circ}$C using an Agilent 1260 Infinity Series GPC/SEC system equipped with Agilent PLGel 5 μm guard column (7.5 × 50 mm) and two Agilent PLGel 5 μm MIXED-D columns (molecular weight range of 450,000 – 500 g mol^{-1}) with a differential refractive index detector (Agilent 1260 Infinity Refractive Index Detector) and an ultraviolet detector (Agilent 1260 Infinity Variable Wavelength Detector). Dichloromethane was used as the eluent at a flow rate of 1 mL min^{-1}. The SEC system was calibrated using seven poly(MMA) standards in the range of 330,000 to 1850 g mol^{-1}. Theoretical molecular weight ($M_{n,th}$) was calculated according to equation 1:

$$M_{n,th} = \frac{[Monomer]_0}{[RAFT]_0} \times M_{Monomer} \times c + M_{RAFT}$$

(1)

where $M_{Monomer}$ and M_{RAFT} correspond to the molecular weight of the monomer and RAFT agent respectively and c is the fractional conversion. In the case of the alkyl CA polymerizations carried out in the presence poly(MMA), [RAFT] refers to the poly(MMA) macroRAFT in this equation.

Mass spectrometry was carried out at the Mass Spectrometry Facility, School of Chemistry, University College Dublin (Ireland) using the GCT premier on chemical ionization mode (CI^{+}).

Precautions: Stringent acidification is required to prevent inadvertent anionic polymerization of alkyl CAs; glassware used for polymerizations was soaked in dilute sulfuric acid, rinsed with acetone, and oven-dried prior to use. Prior to the polymerizations, 1,3-propanesultone was added as an anionic stabilizer[19] at a level of 0.01% $^{w}/_{w}$. Commonly used anionic stabilizers such as acetic and chloroacetic acids were avoided as these can act as chain transfer agents.[20] After precipitation in polar non-solvents, degradation of poly(CA)s prepared by radical polymerization is reported to be less than if prepared through anionic polymerization.[21,22] Nevertheless, the poly(CA)s in the present work were precipitated in cold methanol containing 0.05% $^{w}/_{v}$ MSA as a precaution to prevent degradation of the isolated polymer while also inhibiting the anionic polymerization of any residual monomer.

Representative example of RAFT polymerization using low molecular weight RAFT agents

ECA (5 g, 0.040 mol), AIBN (3.3 mg, 0.020 mmol), CPDB (22.3 mg, 0.100 mmol) and 1,3-propanesultone (1 mg, 0.0082 mmol) in toluene (5.8 mL) were heated at 60 $^{\circ}$C.

Representative synthesis of poly(MMA) MacroRAFT agent

MMA (75 g, 0.749 mol), AIBN (0.492 g, 3.0 mmol) and CPDB (3.315 g, 15 mmol) in toluene (80 mL) were heated at 65 $^{\circ}$C. After 6.5 h, 41.80 g of dried polymer was isolated with M_n = 6,600 and Đ = 1.10. The M_n of the macroRAFT used in the diblock synthesis varied.

Representative example of the synthesis of the diblocks

ECA (22 g, 0.176 mol), ACN (9.5 mg, 0.039 mmol), poly(MMA)-RAFT (11.605 g, 1.758 mmol) and 1,3-propanesultone (11 mg, 0.090 mmol) in toluene (58 mL) was divided into equal parts, and heated at 95 $^{\circ}$C for various times.

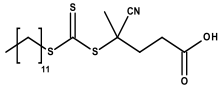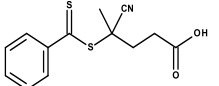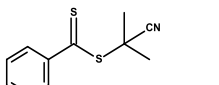*Representative example of the synthesis of the triblocks*

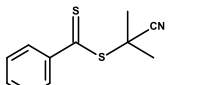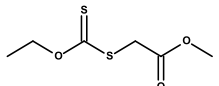MMA (11.060 g, 0.110 mol), ACN (9 mg, 0.037 mmol) and poly(MMA)-*b*-poly(ECA)-RAFT (2.100 g, 0.184 mmol) were heated at 90 ^{o}C for 2.5 h.

RESULTS AND DISCUSSION

RAFT polymerization of ECA using low molecular weight RAFT agents

Our preliminary investigation utilized the commercial RAFT agents 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl]pentanoic acid (CDSPA), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTPA) and cyanoisopropyl dithiobenzoate (CPDB), which are typically used to control the polymerization of methacrylates and methacrylamides, and methyl (ethoxycarbonothioyl)sulfanyl acetate (MESA), which is often used to control the polymerization of vinyl acetate.[23,24] In all these cases, controlled/living character was not achieved (Table 1) with M_n being vastly greater than $M_{n,th}$ and Đ relatively high. MESA, a dithiocarbonate, was chosen since dithiocarbamates caused inadvertent anionic polymerization of the CA.

The use of MESA did not result in any improvement with an even larger discrepancy between M_n and $M_{n,th}$ and higher dispersity (Đ = 1.67).

RAFT Agent	Temp.	[AIBN]/[RAFT]/[ECA]	Conv. (%)	M_n	$M_{n,th}$	Đ
CDSPA	60 ^{o}C	1 /10 / 1000	32	72750	4400	1.52
CTPA	60 ^{o}C	1 / 5 / 1000	41	72150	10550	1.35
CPDB	60 ^{o}C	1 / 5 / 2000	32	95250	16250	1.40
CPDB	80 ^{o}C ^{a}	1 / 5 / 500	41	36050	5350	1.49
MESA	60 ^{o}C	1 / 19.5 / 3300	33	101150	7150	1.67

[ECA] = 3.82 M in toluene. ^{a}ACN as initiator.

**TABLE 1.** Low MW RAFT-agent mediated polymerizations of ECA.

RAFT polymerization of ECA using poly(MMA) MacroRAFT agent

Given polymerization of CAs involves a conjugated tertiary propagating radical, it seemed plausible that a reasonably bulky macroRAFT agent with a leaving group ability greater than or at least comparable to, that of the poly(CA) radical is required. Although the dispersities in Table 1 are relatively high for all of the RAFT agents evaluated, there is greater discrepancy between M_n and $M_{n,th}$ for CDSPA and MESA than for the dithiobenzoates CTPA and CPDB. Therefore, as the next step, a macroRAFT agent was chosen based on poly(MMA) derived from CPDB ($M_n \approx 6,000$ g mol^{-1} and $Đ \approx 1.10$). The polymerization temperature was increased to 90 ^{o}C to ensure sufficiently rapid fragmentation of the intermediate polymeric RAFT adducts.

Polymerizations of ECA were carried out using 1,1'-azobis(cyclohexanenitrile) (ACN) as initiator and [macroRAFT]$_0$/[ACN]$_0$ = 5 with two different [ECA]$_0$/[macroRAFT]$_0$ ratios of 45 and 90. Polymerizations proceeded to high conversions of 65 ([ECA]$_0$/[macroRAFT]$_0$ = 45) and 85% ([ECA]$_0$/[macroRAFT]$_0$ = 90) within 2.5 h (Fig. 2a). The MWDs were relatively narrow and monomodal for both [ECA]$_0$/[macroRAFT]$_0$ ratios ($Đ$ = 1.12-1.15 and 1.26-1.29), shifting to higher molecular weights with increasing conversion, indicating controlled/living character (Fig. 3a). The number-average molecular weights (M_n) increased with conversion, but deviated somewhat from $M_{n,th}$ (Fig. 4a). It must be pointed out that the molecular weights are relative to linear poly(MMA) standards, which invariably introduces a level of error.

In an attempt to further improve the control/livingness, the initiator concentration was lowered from [macroRAFT]$_0$/[ACN]$_0$ = 5 (for the above ECA polymerizations) to 20 and 45 at 90 ^{o}C and 95 ^{o}C, respectively, for [ECA]$_0$/[macroRAFT]$_0$ = 100. In RAFT polymerization, the number of dead chains via bimolecular termination is equal to the number of radicals generated from the initiator that initiate polymer chains (if termination occurs exclusively via disproportionation, half that number of dead chains is generated compared to the case of combination only).[25] The two polymerizations using the higher [macroRAFT]$_0$/[ACN]$_0$ ratios proceeded at a similar rate to high conversions (Fig. 2a) with molecular weights increasing gradually with conversion (Fig. 4b), but tended to deviate towards M_n values lower than $M_{n,th}$. Surprisingly, the lower initiator concentration resulted in lower M_n at a given conversion, which may partly originate in the higher temperature (resulting in a greater number of chains due to more initiator decomposition) with this 95 ^{o}C polymerization also being marginally faster. The MWDs remained narrow throughout ($Đ$ = 1.12-1.25 and 1.13-1.21 for [macroRAFT]$_0$/[ACN]$_0$ = 20 and 45), although there is some high molecular weight broadening at intermediate to high conversion (Fig. 3b).
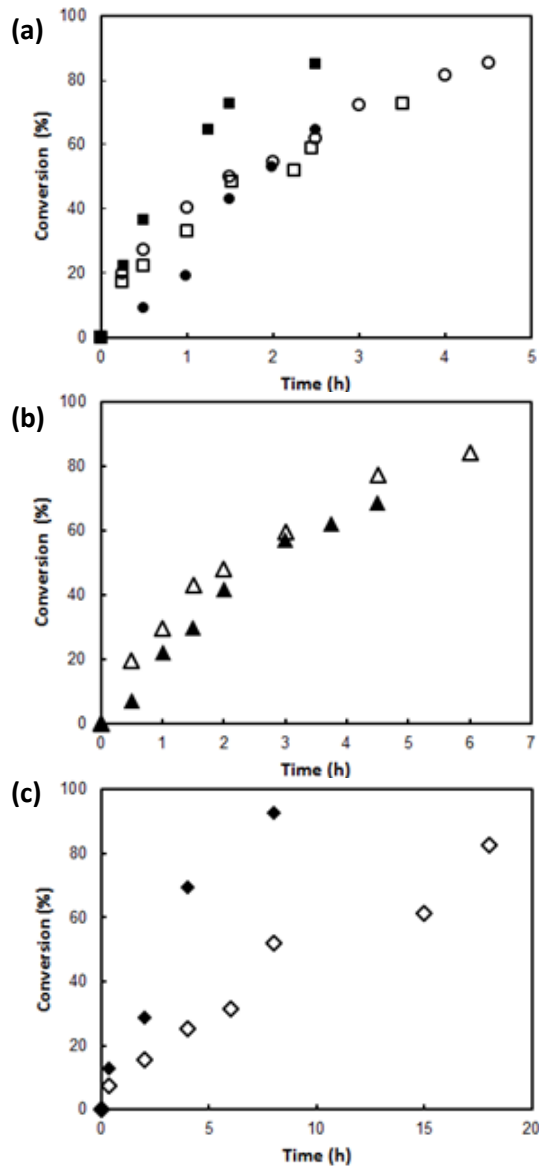
FIGURE 2 Conversion versus time plot for the RAFT polymerization of CAs in toluene in the presence of poly(MMA)-RAFT (macroRAFT) at 90 $^\circ$C unless otherwise stated. **(a)** ECA: $[ECA=1.11M]_0/[macroRAFT]_0/[ACN]_0 = 225/5/1$ (●); $[ECA=2.23M]_0/[macroRAFT]_0/[ACN]_0 = 450/5/1$ (■); $[ECA=2.23M]_0/[macroRAFT]_0/[ACN]_0 = 2000/20/1$ (□); $[ECA=2.23M]_0/[macroRAFT]_0/[ACN]_0 = 4500/45/1$ (○) at 95 $^\circ$C. **(b)** nBCA: $[nBCA=0.98M]_0/[macroRAFT]_0/[ACN]_0 = 225/5/1$ (▲); $[nBCA=1.95M]_0/[macroRAFT]_0 = 900/10/1$ (△) **(c)** $[PECA=0.72M]_0/[macroRAFT]_0/[ACN]_0 = 225/5/1$ (◊); $[PECA=0.72M]_0/[macroRAFT]_0/[ACN]_0 = 900/20/1$ (♦) at 110 $^\circ$C.
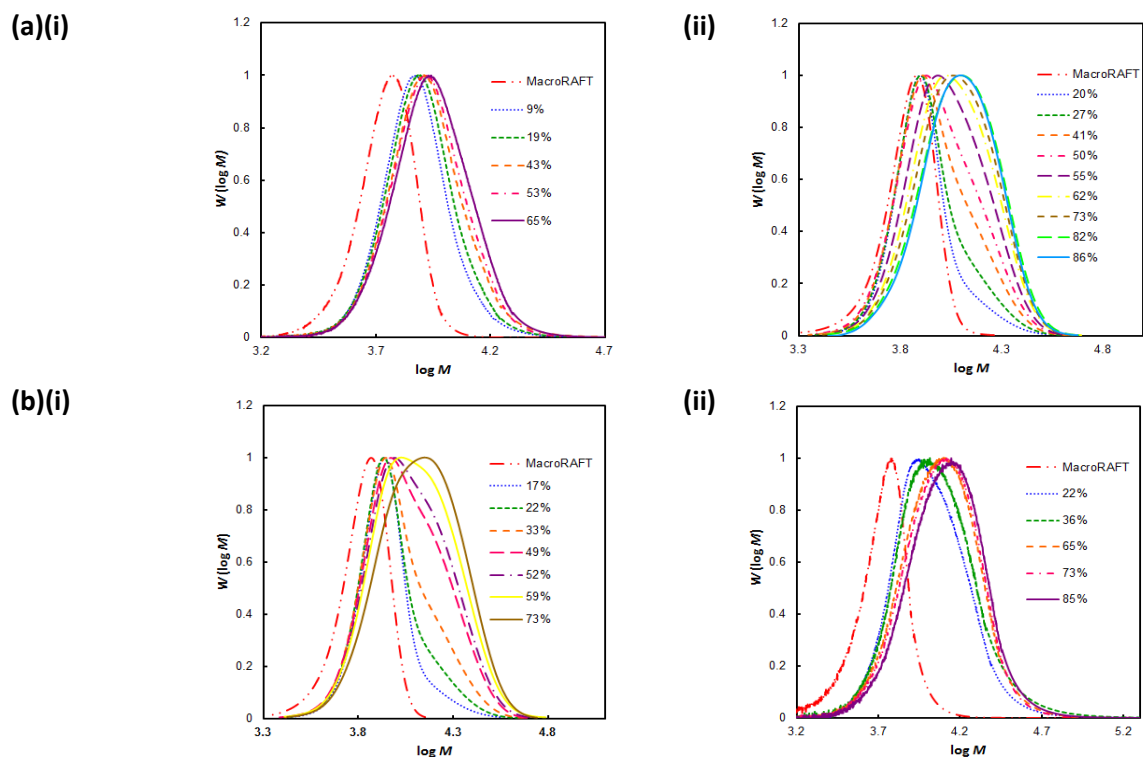
FIGURE 3 MWDs for the RAFT polymerization of ECA in toluene in the presence of poly(MMA)-RAFT (macroRAFT). **(a)** Polymerizations at 90 ^{o}C using (i) $[ECA]_0/[macroRAFT]_0/[ACN]_0$ = 225/5/1 (ii) $[ECA]_0/[macroRAFT]_0/[ACN]_0$ = 450/5/1 **(b)** Polymerizations using lower initiator concentrations with (i) $[ECA]_0/[macroRAFT]_0/[ACN]_0$ = 2000/20/1 at 90 ^{o}C (ii) $[ECA=2.23M]_0/[macroRAFT]_0/[ACN]_0$ = 4500/45/1 at 95 ^{o}C
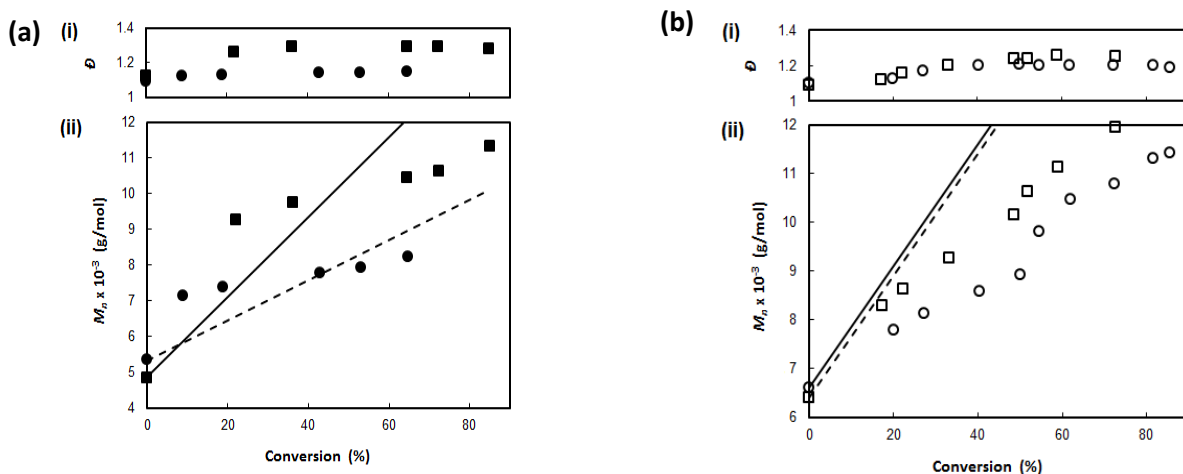
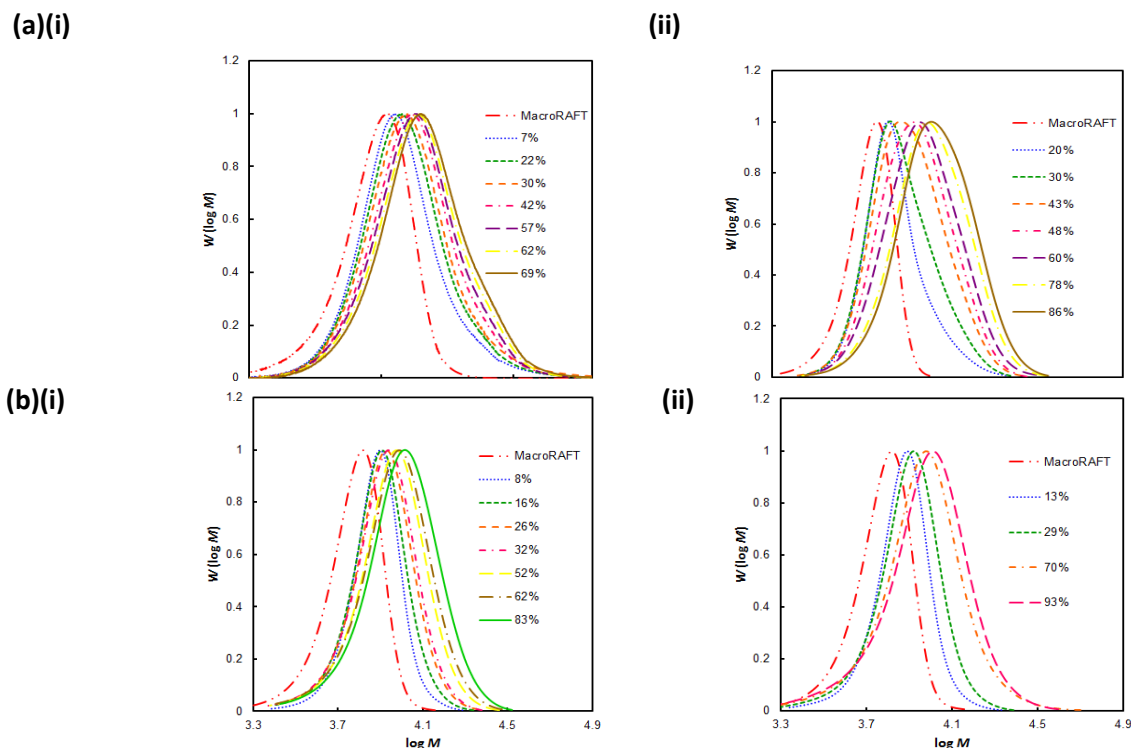
FIGURE 4 RAFT polymerization of ECA in toluene in the presence of poly(MMA)-RAFT (macroRAFT) at 90 ^{o}C (unless otherwise stated) (i) Đ and (ii) M_n versus conversion. **(a)** Polymerizations used $[ECA]_0/[macroRAFT]_0/[ACN]_0$ = 225/5/1 (●) with $M_{n,th}$ short dashed line and $[ECA]_0/[macroRAFT]_0/[ACN]_0$ = 450/5/1 (■) with $M_{n,th}$ continuous line and **(b)** Polymerizations used $[ECA]_0/[macroRAFT]_0/[ACN]_0$ = 2000/20/1 (□) with $M_{n,th}$ short dashed line and at 95 ^{o}C $[ECA]_0/[macroRAFT]_0/[ACN]_0$ = 4500/45/1 (○) with $M_{n,th}$ continuous line using a macroRAFT of M_n = 6,400 and 6,600 respectively.

RAFT polymerization of nBCA and PECA using MacroRAFT agent

RAFT polymerizations of alternative CA monomers were also investigated; *n*BCA was polymerized at 90 °C with $[nBCA]_0/[macroRAFT]_0$ = 45 and 90, and $[macroRAFT]_0/[ACN]_0$ = 5 and 10, respectively. Polymerizations proceeded to 69 and 86% conversions in 5-6 h (Fig. 2b), the somewhat lower rate presumably caused by the lower k_p of *n*BCA compared to that of ECA.[11,12] In both cases, the MWDs were monomodal and narrow ($Đ$ = 1.13-1.16 and 1.15-1.24 for $[nBCA]_0/[macroRAFT]_0$ = 45 and 90, respectively) throughout, and shifting to higher molecular weight with increasing conversion (Fig. 5a). The linear evolution of M_n with conversion for $[nBCA]_0/[macroRAFT]_0$ = 90 with molecular weights almost double those using $[nBCA]_0/[macroRAFT]_0$ = 45 is consistent with good control/livingness (Fig. 6a).

RAFT polymerization of the solid CA monomer PECA was examined using 0.72 M solutions in toluene. Polymerization at 90 °C using $[PECA]_0/[macroRAFT]_0$ = 45 and $[macroRAFT]_0/[ACN]_0$ = 5 reached 83% conversion in 18 h. The polymerization was slower due to the use of dilute solutions in toluene (Fig. 2c). The MWDs remained narrow and monomodal ($Đ$= 1.08-1.18) throughout (Fig. 5b), with M_n increasing with conversion (Fig. 6b). In order to increase the rate, the polymerization was also carried out at a higher temperature of 110 °C, resulting in a three-fold increase in rate to reach 92% conversion in 8 h (Fig. 2c). Molecular weights grew linearly with conversion with $Đ$ remaining low (1.10-1.25; Fig. 6b). However, at both temperatures, the M_n values were significantly lower than $M_{n,th}$ at conversions beyond ~20%.

(a)(i)

(ii)

(b)(i)

(ii)

FIGURE 5 MWDs for the RAFT polymerization in the presence of poly(MMA)-RAFT (macroRAFT) of **(a)** *n*BCA in toluene at 90 °C (i) $[nBCA]_0/[macroRAFT]_0/[ACN]_0$ = 225/5/1; (ii) $[nBCA]_0/[macroRAFT]_0/[ACN]$ = 900/10/1 and **(b)** PECA in toluene (i) $[PECA]_0/[macroRAFT]_0/[ACN]_0$ = 225/5/1 at 90 °C; (ii) $[PECA]_0/[macroRAFT]_0/[ACN]_0$ = 900/20/1 at 110 °C.
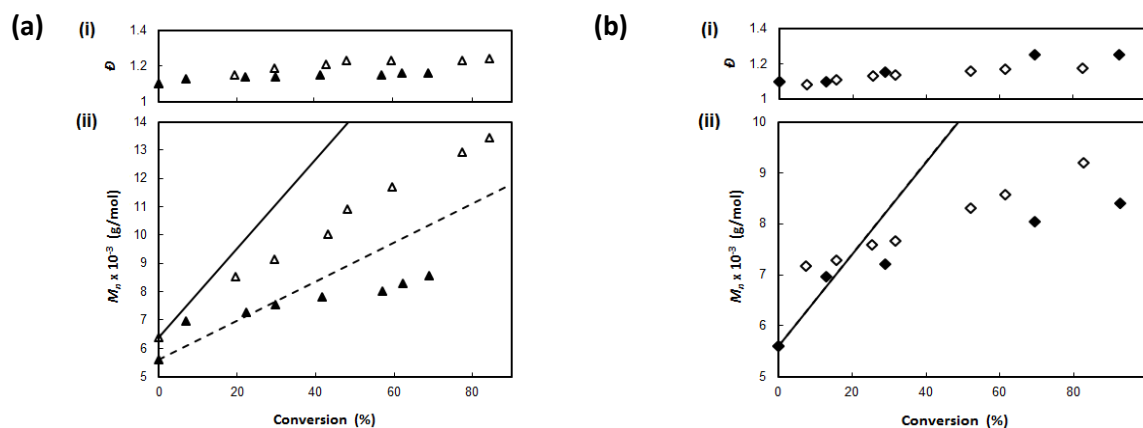
FIGURE 6 RAFT polymerization in the presence of poly(MMA)-RAFT (macroRAFT) of **(a)** nBCA in toluene at 90 $^{\circ}$C and **(b)** PECA in toluene (i) $Đ$ and (ii) M_n versus conversion. Polymerizations used $[n\text{BCA}]_0/[\text{macroRAFT}]_0/[\text{ACN}]_0 = 225/5/1$ (▲) with $M_{n,th}$ short dashed line and $[n\text{BCA}]_0/[\text{macroRAFT}]_0/[\text{ACN}] = 900/10/1$ (△) with $M_{n,th}$ continuous line. $[\text{PECA}]_0/[\text{macroRAFT}]_0/[\text{ACN}]_0 = 225/5/1$ (◊) at 90 $^{\circ}$C and $[\text{PECA}]_0/[\text{macroRAFT}]_0/[\text{ACN}]_0 = 900/20/1$ (♦) at 110 $^{\circ}$C with Mn,th continuous line.
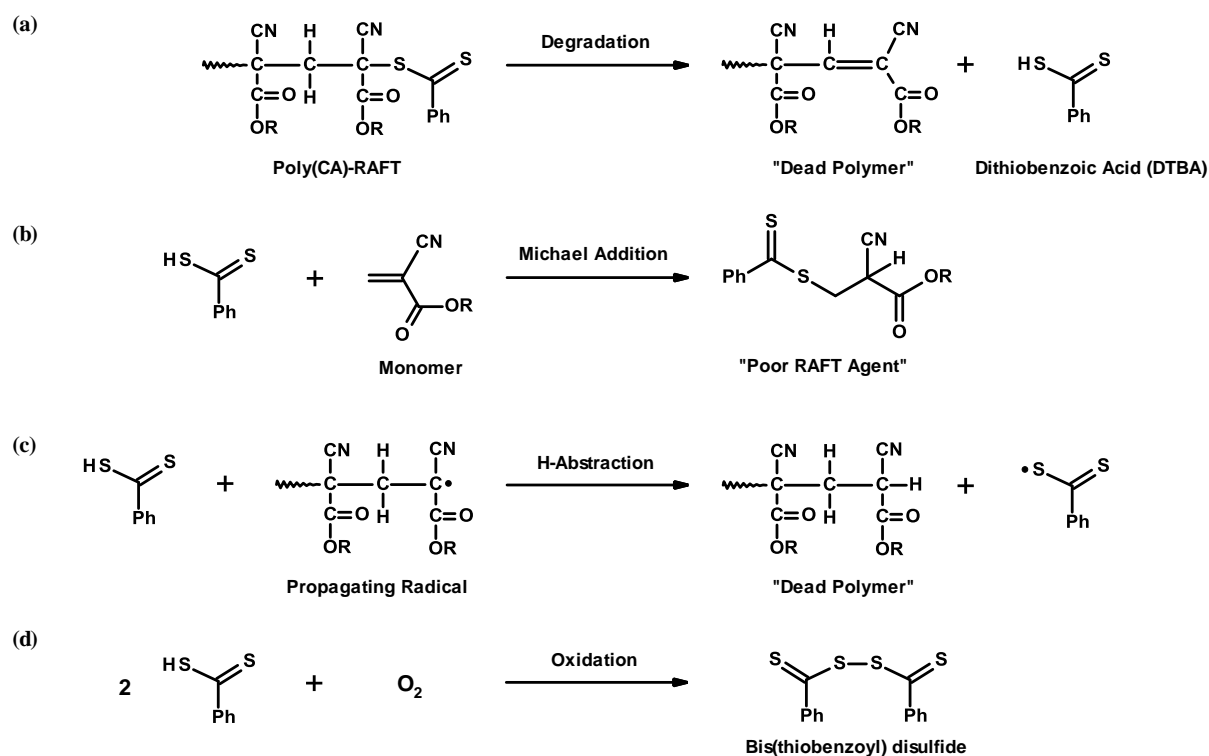

**SCHEME 1** Degradation of poly(CA) macroRAFT and reactivity of DTBA

UV-analysis of livingness.

GPC UV-detection allows for end group analysis as the thiocarbonyl groups absorb in the UV-Vis range, which accounts for the yellow, orange or reddish color of RAFT derived polymers. In order to examine the livingness (RAFT end group retention), the polymers were analyzed by GPC UV-detection at 304 nm (Fig. 7) (GPC data discussed so far correspond to RI detection). At this wavelength, the detector response corresponds to the $\pi \to \pi^*$ transition of the C=S bond of the dithioester functionality,[26,27] and poly(MMA) and poly(CA) repeating units do not absorb. The UV-GPC traces have been normalized to the height of the polymer peak in each case (Fig. 7). The polymer peak remains narrow and shifts to higher molecular weight with increasing conversion. There are however several low molecular weight peaks in the UV-GPC traces which are absent in the RI data, which increase in relative intensity with increasing conversion. Moreover, these low molecular weight peaks are very similar for the three monomers examined (ECA, *n*BCA and PECA) (Fig. 7). It can be inferred that the number of living chains in the polymer peak (around $\log M \approx 4$) is decreasing during the polymerization.

The loss of RAFT end groups was quantified by monitoring the area of the polymer peak in the UV detector response versus time (based on a constant injection volume of GPC samples of fixed wt% polymer, and correcting for the increase in polymer mass relative to the number of end groups with conversion). The resulting normalized UV response (area under the curve), which is proportional to the number of RAFT end groups, was plotted versus time (Fig. 8a) and conversion (Fig. 8b). For all three monomers, the loss of livingness is at least 70% at the end of the polymerization. The plots of UV response versus conversion all follow a very similar trend.
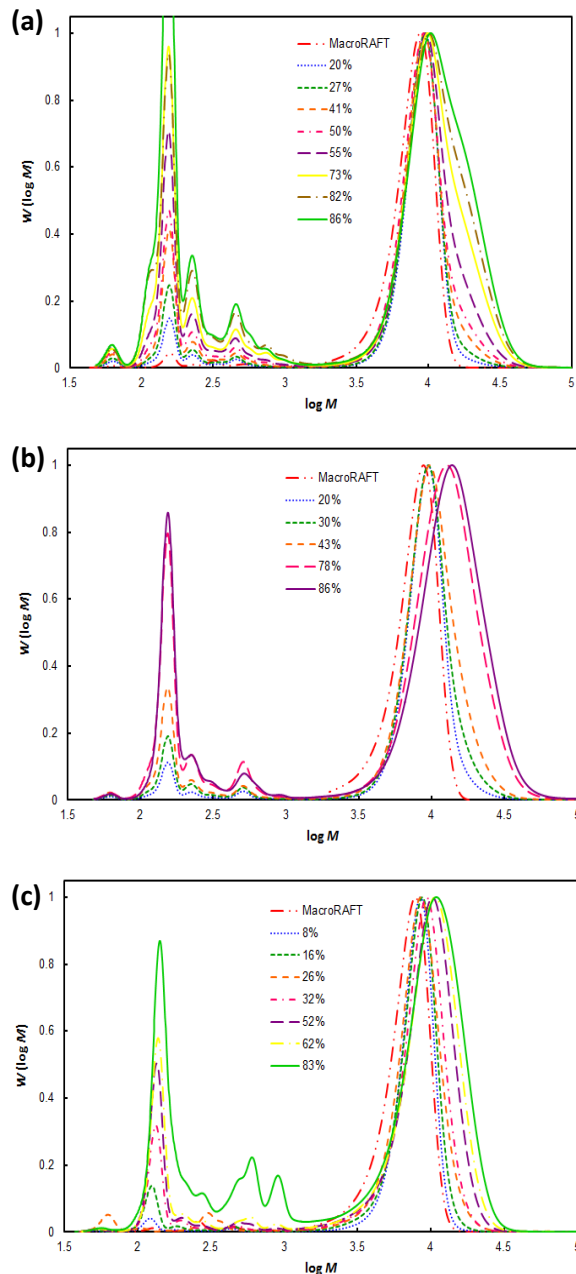

FIGURE 7 UV MWDs at 304 nm for the RAFT polymerization of CA in toluene in the presence of poly(MMA)-RAFT (macroRAFT) (conversions as indicated). Polymerizations using **(a)** $[ECA]_0/[macroRAFT]_0/[ACN]_0$ = 4500/45/1 at 95 $^{\circ}$C **(b)** $[nBCA]_0/[macroRAFT]_0/[ACN]$ = 900/10/1 at 90 $^{\circ}$C and **(c)** $[PECA]_0/[macroRAFT]_0/[ACN]_0$ = 225/5/1 at 90 $^{\circ}$C.

(a)

(b)
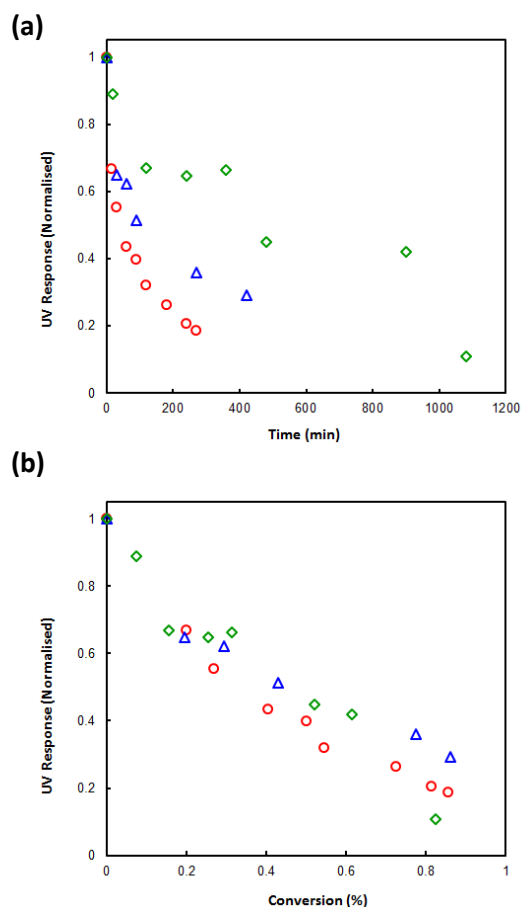
FIGURE 8 Total UV Response from UV-GPC of the polymer peaks versus **(a)** Time and **(b)** Conversion for [ECA=2.23M]$_0$/[macroRAFT]$_0$/[ACN]$_0$ = 4500/45/1 (⭕) at 95 ^{o}C, [nBCA=0.98M]$_0$/[macroRAFT]$_0$/[ACN]$_0$ = 225/5/1 (🔺) at 90 ^{o}C and [PECA=0.72M]$_0$/[macroRAFT]$_0$/[ACN]$_0$ = 225/5/1 (◇) at 90 ^{o}C

Further evidence of the poly(MMA)-b-poly(CA)-RAFT inherent instability was demonstrated when a sample of poly(MMA)-b-poly(ECA)-RAFT was dissolved in toluene and heated at the typical polymerization temperature of 90 ^{o}C for a number of hours with aliquots withdrawn periodically for UV-GPC analysis (Fig. 9) using the same methodology as Figure 8. A steady decrease in the number of polymer RAFT end groups was observed.
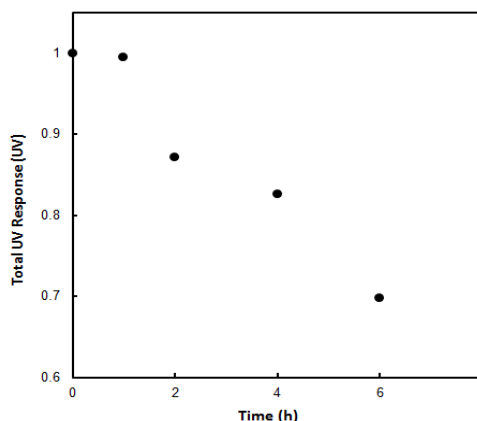
FIGURE 9 Total UV Response of polymer peaks versus time from UV-GPC of poly(MMA)-b-poly(ECA)-RAFT heated in toluene at 90 ^{o}C

Dithioester RAFT agents are particularly susceptible to hydrolysis reactions which eliminate the active end group. This is typically observed in basic media with an increased rate of hydrolysis with increasing pH, and can manifest itself as $M_n > M_{n,th}$.[28,29] Given that the reaction media of the polymerizations reported herein are moderately acidic, the effect of such hydrolysis would be expected to be negligible.

An alternative degradation pathway is proposed for these poly(MMA)-b-poly(CA)-RAFT polymers via an elimination mechanism to generate dithiobenzoic acid (DTBA) and polymer with an unsaturated end group (Scheme 1a) analogous to the degradation of poly(MMA)-RAFT polymers.[30-32] The prominent low molecular weight peak in the UV-GPC spectra (Fig. 7) has a peak value of 155 g mol^{-1}, which coincides with the molar mass of DTBA.
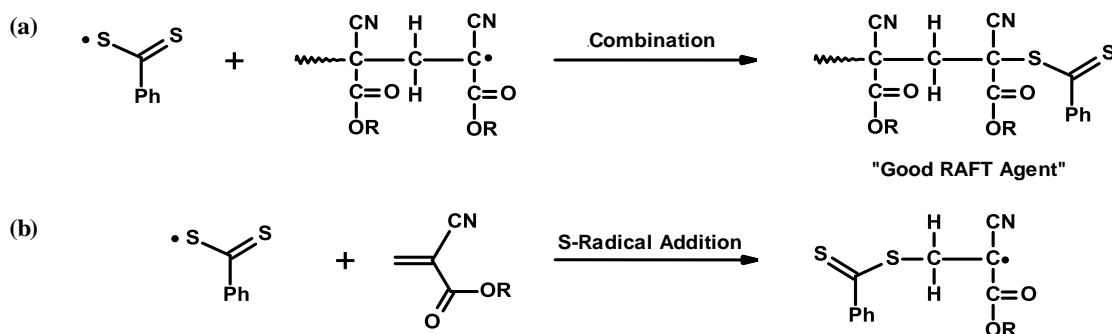
SCHEME 2 Reactions of DTBA radical derived from end-group decomposition

However, this value is obviously prone to significant error given that it is based on poly(MMA) standards and also falls outside the calibrated range of the GPC. Mass spectra of these diblock copolymer mixtures confirmed the presence of DTBA with a sharp peak at *m/z* 153 and 154 g mol^{-1}.[27] It is worth mentioning that the presence of DTBA is also indicated by a strong red color[33] with all CA polymerization mixtures changing from the characteristic RAFT pink color to a red color with time/conversion. The acidity of the methylene at the chain terminus is expected to be enhanced by the inductively electron withdrawing nitrile and ester functionalities leading to formation of an unsaturated end group. The latter is difficult to detect by conventional techniques (such as NMR) due to its quaternary nature or full substitution (with CN and COOR).

The DTBA formed via RAFT end group decomposition can add to a CA monomer via a Michael addition reaction as reported for acrylates and MMA (Scheme 1b).[34] This would generate an ineffective RAFT agent with poor primary leaving group, which would be slow to fragment in the RAFT process. However, it cannot be excluded that the formation of low molecular weight species detected in UV-GPC traces could be to some extent attributable to species derived from the chain transfer via the Michael adduct. More importantly, the DTBA

can itself act as a chain transfer agent through the radical abstraction by a propagating radical of the labile-H from the thiol moiety to give a hydrogen terminated dead polymer chain and the reactive Ph-C(=S)-S• radical species (Scheme 1c). This S-radical can then combine with a propagating radical to give a dithioester with a tertiary polymeric leaving group and thereby generate a "good" RAFT agent (Scheme 2a), as proposed for controlled/living RAFT polymerizations of MMA using DTBA as mediator,[34-36] and/or the DTBA radical can add to a CA monomer (Scheme 2b). This might seem unlikely given the expected electrophilic nature of the DTBA radical and the electron deficient double-bond of the CA monomer, however dithiocarbamates are known iniferters for MMA polymerization[37] and similarly electrophilic radical fragments of benzoyl peroxide are known to add to CA monomer.[19] Despite this, addition to monomer will be slow as the transfer constant is predicted to be low and even with an addition of a single monomer unit (or a few monomer units) there is a high probability that termination with other radicals in the system will occur rather than extensive propagation.[38] Such termination reactions would generate "poor" difunctional (combination) and mono-functional RAFT agents (disproportionation) that may in turn participate in further reactions (Scheme 3).
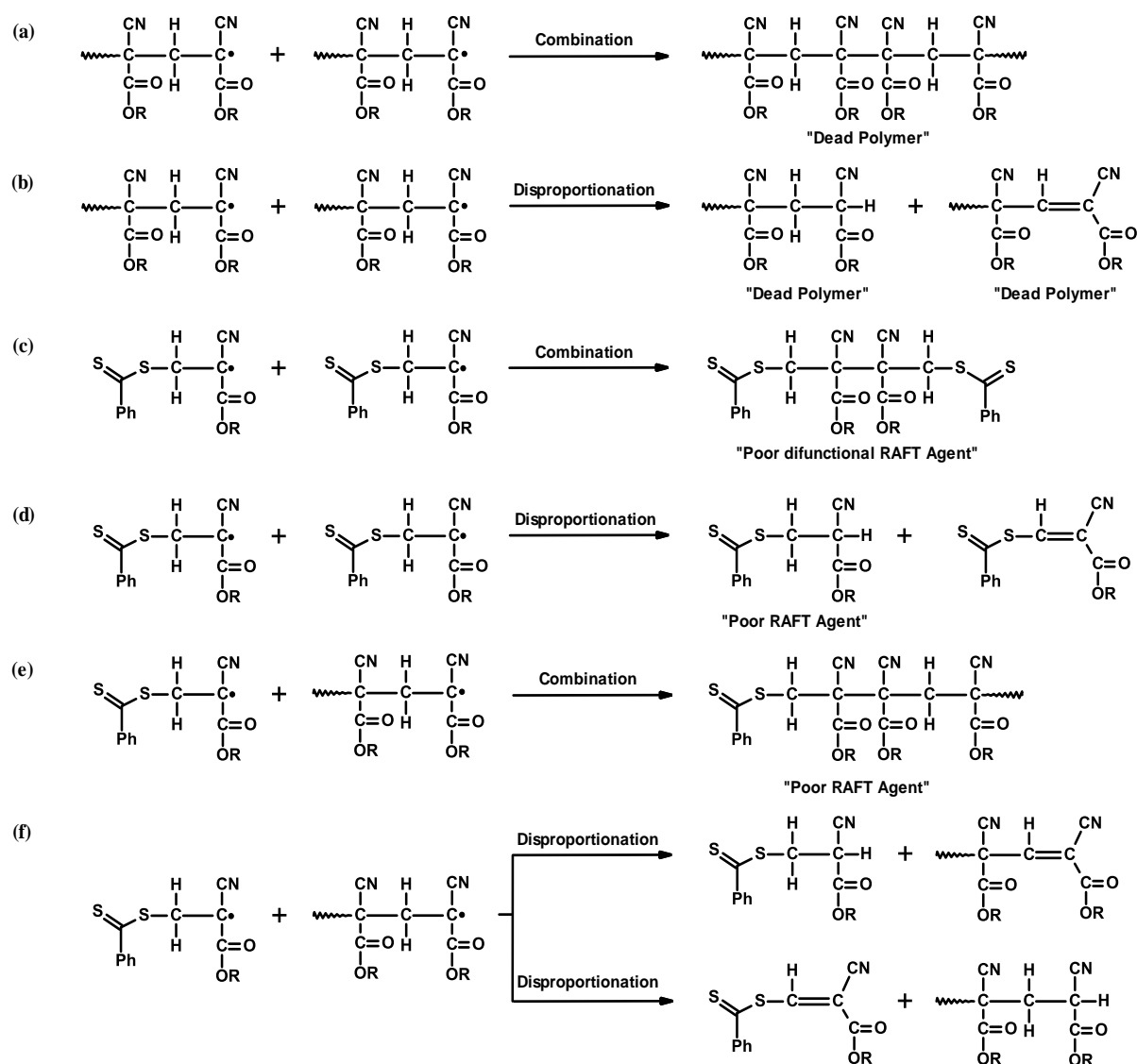
SCHEME 3 Propagating radical termination reactions.

The above set of reactions have the net effect of transforming a polymer chain with a RAFT end group to a dead polymer chain and a low molecular weight species (DTBA; Scheme 1a), which is proposed to ultimately lead to an increase in the number of chains via the reaction pathways starting with the generation of DTBA. This exchange of polymer RAFT end groups to give non-living polymers and newly formed living polymers increases the number of chains, which in turn causes a steady increase in $Đ$ with conversion, which is what is experimentally observed (Fig 4 and Fig 6). This is in contrast to the typical decrease in $Đ$ with increasing conversion that would be expected in a standard RAFT polymerization.[39] Furthermore, the increase in the number of chains accounts for the 2-3 fold deviation of M_n below $M_{n,th}$ observed in these RAFT mediated alkyl CA polymerizations.
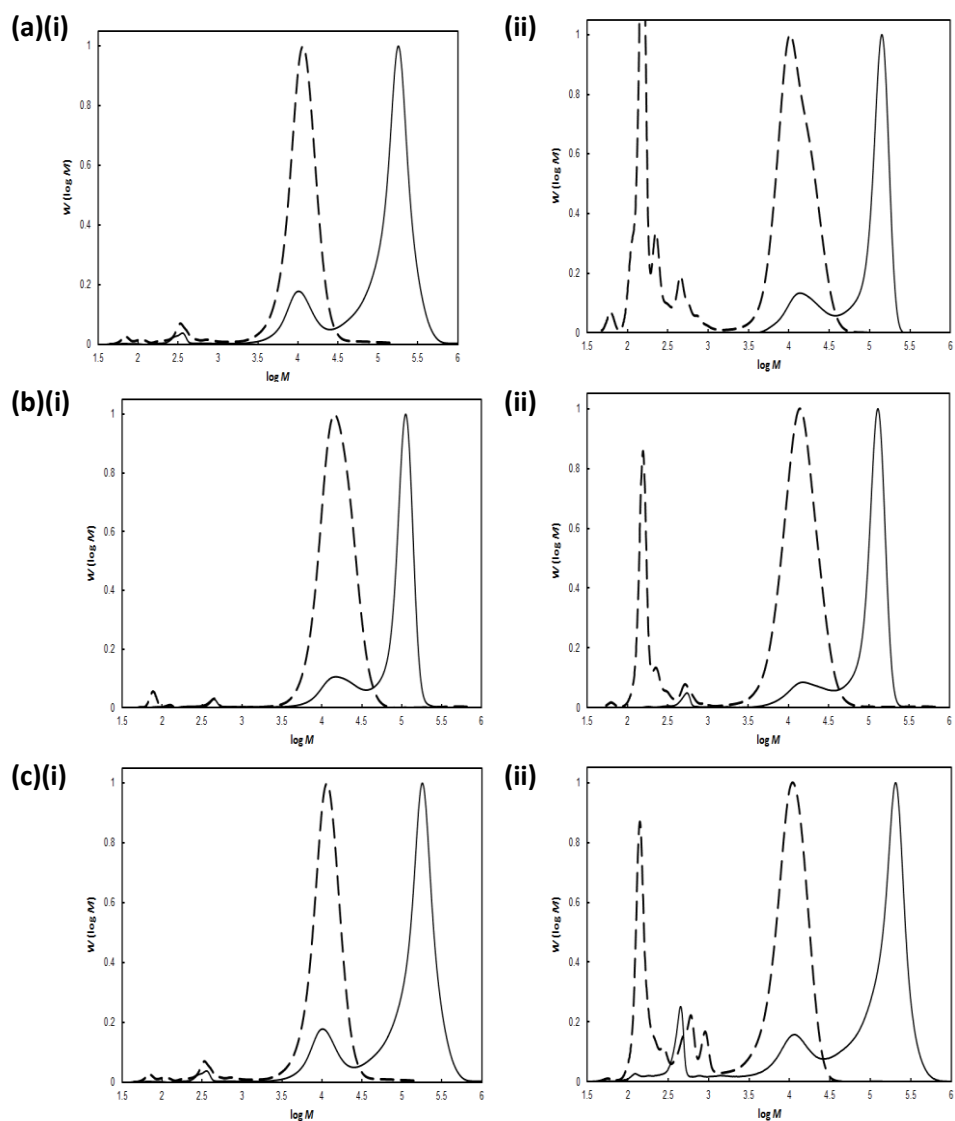
FIGURE 10 (i) RI and (ii) UV GPC/SEC distributions for the chain extensions of poly(MMA)-*b*-poly(CA)-RAFT (dashed line), which is then extended with MMA in bulk at 90 $^{\circ}$C, where $[MMA]_0/[diblock]_0 = 600$ and $[diblock]_0/[ACN]_0 = 5$ to give the triblock (continuous line) **(a)** Extension of ECA containing diblock (from Fig 3(b)(ii) at 85.5% conversion) at 47% conversion. **(b)** Extension of *n*BCA containing diblock (from Fig 5(a)(ii) at 86% conversion) at 51% conversion. **(c)** Extension of PECA containing diblock (from Fig 5(b)(i) at 82.5% conversion) at 69% conversion.

Chain extension of poly(MMA)-b-poly(CA)-RAFT with MMA

Formation of non-living polymer chains was further evidenced by chain extensions of the poly(MMA)-*b*-poly(CA)-RAFT diblock copolymers with MMA in bulk at 90 $^{\circ}$C using $[MMA]_0/[diblock]_0$ = 600 and $[diblock]_0/[ACN]_0$ = 5 (Fig. 10). In all three cases, the resulting RI-GPC MWDs clearly show generation of triblock copolymer poly(MMA)-*b*-poly(CA)-*b*-poly(MMA)-RAFT, but a significant portion of the original diblock copolymers are not chain extended. GPC with UV detection revealed that these non-extended chains not only comprised dead chains as a result of loss of RAFT end groups (Scheme 1), but also consisted of chains that possessed the thiocarbonyl functionality, consistent with the formation of "poor" RAFT agents (Scheme 1 and 3). UV detection also showed essentially negligible amounts of low molecular weight material (unlike the CA polymerizations, Fig. 7) for the chain extensions of the ECA and *n*BCA blocks (save for PECA, but still substantially less than for the CA polymerizations). These data thus support the notion that RAFT end group decomposition occurs at a markedly higher rate for CA polymers than for poly(MMA).

CONCLUSIONS

The first study of controlled/living character for polymerization of cyanoacrylates is reported using a poly(MMA) macroRAFT. The synthesis of diblock (and triblock) copolymers of this challenging monomer class by radical polymerization has not previously been reported. Control was however far from ideal, as molecular weights tended to deviate towards values lower than $M_{n,th}$, which was attributed to degradation of the formed polymer during polymerization. The poly(MMA)-*b*-poly(CA)-RAFT formed appears to be inherently unstable with self-elimination of the RAFT end group occurring rapidly as the polymer is formed to generate DTBA. This degradation was not apparent by RI detection of GPC analyses but could be observed by UV detection and was evident for all three cyanoacrylate monomers examined. The polymerization process is thought to be further complicated by combination and disproportionation reactions of radicals formed during decomposition.

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