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# Influence of reaction parameters on the synthesis of hyperbranched polymers via reversible addition fragmentation chain transfer (RAFT) polymerization

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**Abstract**

The synthesis of hyperbranched poly(methyl methacrylate) (PMMA) via reversible addition fragmentation chain transfer (RAFT) polymerization was investigated by varying the ratio chain transfer agent (CTA): monomer (methyl methacrylate, MMA): brancher (ethylene glycol dimethyl methacrylate, EGDMA): free radical initiator (AIBN) at various temperatures (50, 55, 60, 65, 70 °C). The rate of polymerization was observed to increase with temperature and concentration in brancher, whilst it was lowered by an increase in chain transfer agent concentration. The molecular weight of the samples increased with the ratios brancher: CTA and monomer: CTA. The polydispersity of the samples increase with conversion, as the level of branching increases. At fixed concentration in brancher, an increase of CTA concentration led to polymers with lower PDI. The variation of enthalpy ($\Delta\bar{H}_m$) and entropy ($\Delta\bar{S}_m$) relative to the monomer reaction were calculated, and it was observed that an increase in the brancher concentration induced an increase in both $\Delta\bar{H}_m$ and $\Delta\bar{S}_m$, whilst lower CTA concentrations led to an increase in $\Delta\bar{S}_m$. The variation in Gibbs energy for the monomer reaction ($\Delta\bar{G}_m$) was calculated at 60 °C, and results confirmed the presence of a retardation effect when increasing CTA concentration generally observed in RAFT polymerization.

*Keywords:* Hyperbranched; Reversible addition fragmentation chain transfer (RAFT) polymerization; Methacrylate

## 1. Introduction

Recently, the development of facile, versatile, and cost-effective routes for the synthesis of branched or hyperbranched polymers have received a renewed interest, following work published by Sherrington's group. Their strategy involves the conventional free radical polymerization of a vinyl monomer, in the presence of a multifunctional vinyl comonomer and a chain transfer agent to prevent crosslinking [1–6]. Besides using conventional chain transfer agents in the synthesis of branched polymers, Sherrington's group, in collaboration with Armes' group, also applied copper mediated living radical polymerization (LRP) and group transfer polymerization (GTP) to the synthesis of soluble branched polymers in facile one-pot reactions, and obtained well-controlled hyperbranched architectures [4]. Following this work, we investigated the use of reversible addition fragmentation chain transfer (RAFT) polymerization to achieve similar results [7]. In the copolymerization of methyl methacrylate (MMA) with ethylene glycol dimethyl methacrylate (EGDMA) mediated by cyanoisopropyl dithiobenzoate (CPDB), we observed that RAFT polymerization not only prevented cross-linking, but also permitted to produce hyperbranched polymers, with a ratio chain transfer agent (CTA): brancher $<2$. We also demonstrated that the hyperbranched polymers could be reinitiated to mediate further the polymerization of a second monomer (styrene), leading to a star-shaped macromolecule, with a hyperbranched core and poly(styrene) arms [8]. This approach, although leading to less well-defined structures, was simpler to undertake than other studies in which dendrimers were modified into multifunctional chain transfer agents to mediate RAFT polymerization [8–10].

A striking observation from the RAFT polymerization

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literature is that there is very little thermodynamic information on the technique. Indeed, the most complete thermodynamic study on the RAFT system was undertaken by Coote and co-workers, who used ab initio molecular orbital calculations to determine the barriers for the fragmentation of chain transfer agent intermediate radicals [11–18]. Computational quantum chemistry was used to study the rate retardation in cumyl dithiobenzoate mediated polymerization of styrene [11] and methyl acrylate [13] and the xanthate mediated polymerization of vinyl acetate [16]. Furthermore, studies of the effects of substituents on the addition and fragmentation reactions in prototypical systems and polymer-related systems were undertaken [13,15, 17,18].

In this communication, we report the thermodynamic study we undertook during the production of hyperbranched PMMA. We report here our findings on the copolymerization of MMA with EGDMA, mediated by RAFT, as a follow up of our previous article on their synthesis.

## 2. Experimental section

### 2.1. Materials

All monomers, solvents, and other reagents were purchased from Aldrich at the highest purity available and used as received unless otherwise stated. Methyl methacrylate (MMA, 99%), ethylene glycol dimethacrylate (EGDMA, 98%) and styrene (99%) were filtered before use through an activated basic alumina (Brockmann I) column to remove radical inhibitors. Azobis (isobutyronitrile) (AIBN, 99%) was recrystallized twice from chloroform–methanol. cyanoisopropyl dithiobenzoate (CPDB) was synthesized following a previously reported preparation [19].

### 2.2. $^1$H NMR spectroscopy

$^1$H NMR spectra were recorded on a 400 MHz Bruker UltraShield spectrometer, with $CDCl_3$ as the solvent and reference.

### 2.3. Size exclusion chromatography

Molecular weight and molecular weight distributions were determined by size exclusion chromatography (SEC) at ambient temperature using a system equipped with a Polymer Laboratories 5.0 μm-bead-size guard column ($50\times7.5$ mm$^2$) and two Polymer Laboratories 5.0 μm MIXED-C columns (molecular weight range of 2,000,000–500 g/mol) with a differential refractive index detector (Shodex, RI-101). Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min$^{-1}$, and toluene as a flow rate marker. All molecular weight data are based on calibration using linear poly(methyl methacrylate) as standards (molecular weight range of 1,944,000–1020 g/mol), and therefore are not the exact molecular weight of the sample, but relative variations between samples can be assessed.

### 2.4. Syntheses of hyperbranched PMMAs via RAFT polymerization

MMA, ethylene glycol dimethyacrylate (EGDMA), and AIBN were added to a solution of dried toluene (toluene: MMA = 1:4 in weight) in 10 mL test tubes, following the mole ratio quoted in Table 1. Each tube was capped with a rubber septum, placed in an ice bath and flushed with nitrogen for 10 min to remove oxygen. The polymerization reactions were conducted for 18 h, with reaction temperatures set to 50, 55, 60, 65, and 70 °C. The resultant products were analyzed by $^1$H NMR to establish the monomer conversions. The molecular weight and molecular weight distributions were determined by SEC. In order to acquire information on chain structures and on the thermal properties of the hyperbranched polymers, the products were precipitated in hexane and analyzed by $^1$H NMR spectroscopy.

Typical polymerization (CPDB:MMA:EGDMA:AIBN = 3:100:5.85:0.3): CPDB (660 mg, $3.0\times10^{-3}$ mol), MMA (10.0 g, 0.10 mol), EGDMA (1.15 g, $5.8\times10^{-3}$ mol) and AIBN (49.0 mg, $0.3\times10^{-3}$ mol) were added to a solution of dried toluene (40.0 g) and 8 g of this solution were sampled in $6\times10$ mL test tubes. Each tube was capped with a rubber septum, placed in an ice bath and flushed with nitrogen for 10 min to remove oxygen. Finally, each tube was placed in a water bath (60 °C) and removed after a predetermined time. The resultant products were analyzed by $^1$H NMR to establish the monomer conversions. The molecular weight and molecular weight distributions were determined by SEC. In order to acquire information on chain structures and on the thermal properties of the hyperbranched polymers, the products were precipitated in hexane and analyzed by $^1$H NMR and DSC. Samples were taken after 8 h (29.5%, $M_n =$ 2800 g/mol, $M_w = 4200$ g/mol, PDI = 1.52, 45% branching), 24 h (72.7%, $M_n = 9300$ g/mol, $M_w = 3900$ g/mol, PDI = 4.19, 45% branching) and 48 h (97.3%,

Table 1
Molar ratios for the copolymerization of methyl methacrylate (MMA) and ethylene glycol methacrylate (EGDMA) mediated by chain transfer agent (CTA) cyanoisopropyl dithiobenzoate in presence of azobis (isobutyronitrile) (AIBN)

| Series | Molar ratios | | | |
|---|---|---|---|---|
| | CTA | MMA | EGDMA | AIBN |
| T1 | 1.00 | 100 | 1.00 | 1.00 |
| T2 | 3.00 | 100 | 1.00 | 1.00 |
| T3 | 3.00 | 100 | 5.85 | 1.00 |
| T4 | 5.04 | 100 | 5.85 | 1.00 |

$M_n = 16{,}300$ g/mol, $M_w = 410{,}100$ g/mol, PDI = 25.2, 90% branching).

$^1$H NMR (CDCl$_3$, 298 K, 400 MHz), $\delta$ (ppm from TMS): 3.51 (s (or t), O–C$H_3$ of MMA), 3.70(s, O–C$H_3$ of EGDMA), 4.05(s, –O–C$H_2$–C$H_2$–O– of crosslinked EGDMA), 4.20, 4.35 (s, –O–C$H_2$–C$H_2$–O– of pendant EGDMA), 6.20 (s, =CH$_2$ of pendant EGDMA), 7.44 (t, *p*-C*H* of 2-(2-cyanopropyl) dithiobenzoate).

### 2.5. Calculation of $\Delta\bar{H}_m$, $\Delta\bar{S}_m$ and $\Delta G_m$ (Eq. (1))

$$\ln(1-x) = \frac{\Delta\bar{H}_m}{RT} - \frac{\Delta\bar{S}_m}{R} \qquad (1)$$

$x$ is the monomer conversion, $\Delta\bar{H}_m$ and $\Delta\bar{S}_m$ are the changes of relative enthalpy and entropy of MMA during the polymerization, respectively, $R$ is the standard gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is the temperature of reaction (K). A plot of $\ln(1-x)$ vs. $1/T$ leads to $\Delta\bar{H}_m$ and $\Delta\bar{S}_m$.

$\Delta G_m$ (Gibbs free energy) is obtained from Eq. (2).

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (2)$$

## 3. Results and discussions

In a previous communication, we reported the use of RAFT polymerization to produce hyperbranched PMMA with ethylene glycol dimethacrylate (EGDMA) as the branching agent [7]. The effects of the molar ratio chain transfer agent (CTA): EGDMA, temperature and polymerization time were studied. The chain architectures were established using $^1$H NMR spectroscopy and we found that the branching process in the MMA–EGDMA system is well controlled by the CTA (Fig. 1). Furthermore, we established that the hyperbranched PMMA could be used as a macro-CTA in order to further polymerized styrene, producing a star-like structure, with the hyperbranched PMMA acting as core and poly(styrene) as arms.

In order to analyze the synthesis of hyperbranched polymers via RAFT polymerization from a thermodynamic viewpoint, a series of experiments was undertaken with four different ratios CTA:MMA:EGDMA:AIBN (Table 1) at five different temperatures (50, 55, 60, 65, and 70 °C), for a fixed reaction time of 18 h. The monomer conversions were determined by $^1$H NMR spectroscopy, by integration of the peaks at 6.2 and 5.7 ppm (=C$H_2$ of unreacted MMA monomer), and 3.5–3.9 ppm (O–C$H_3$ of incorporated and unreacted MMA). A control experiment was also undertaken for each temperature, in which no CTA was added to the reaction mixture. In the latter case, as expected, all reactions showed evidence of early crosslinking, leading to insoluble material. This provides supplementary experimental evidence that the synthesis of soluble branched polymers by free-radical copolymerisation seems impossible when the reaction is taken to high conversion [1].

Fig. 2 shows the change in monomer conversion with temperature, for various ratios of CTA:MMA:EGDMA:AIBN (Table 1), after the same reaction time (18 h). It is clear from Fig. 2 that the monomer conversion is dependent on the reaction temperature, as an increase in polymerization temperatures leads to higher monomer conversions. Furthermore, an increase in CTA concentration leads to a decrease in the monomer conversion (see series T1 and T2, series T3 and T4, Fig. 1). This observation follows the well-known effect of retardation that is usually observed in RAFT polymerizations, the origin of which is the center of an international on-going debate [20,22–24]. By comparing sample from series T2 and T3, one can observe that increasing the concentration of the brancher increases slightly the overall polymerization rate.

Figs. 3 and 4 show the strong influence of varying the CTA and EGDMA concentrations on the evolution of $M_n$ and $M_w$, respectively, whilst increasing the reaction temperature. Series T3 produces the highest $M_n$ and $M_w$ as the ratio EGDMA:CTA (=1.95) is the highest of the set of experiments, whereas series T2, which corresponds to the lowest ratio EGDMA:CTA (=0.33), generates the lowest values for both $M_n$ and $M_w$. Series T1 and T4 have similar ratio EGDMA:CTA, but series T1 reaches higher molecular weights as the ratio MMA:CTA is higher (MMA:CTA = 100 (T1) and 20 (T4)). It is noteworthy that the values of $M_n$ and $M_w$ for both series T1 and T2 seem to reach a maximum at $T = 60$ °C before decreasing, at higher temperatures, whilst series T3 and T4 show a constant increase in molecular weight. We explain this behavior by the lower ratio of EGDMA to MMA. Indeed, in the case of series T1 and T2, branching should only occur at high conversion (i.e. high temperatures, for a fixed reaction time), after most of the double bond available from MMA have reacted to generate well-controlled polymeric chains, and the concentration in pendant double bonds from EGDMA is increased. Branching would therefore result in a slow increase of molecular weight, and the proportion of low molecular weight species would have a strong influence on the overall molecular weight distribution (confirmed by the increase in PDI, Fig. 4), therefore the average molecular weight values should decrease. In the case of series T2 and T3, the highest EGDMA:MMA ratio triggers branching (and crosslinking) earlier in the reaction, and contributes to the loss of control of the molecular weight of individual linear polymeric chains, therefore increasing the molecular weight of the polymers. In the specific case of series T3, the branching degenerates into crosslinking which boosts the molecular weight increase and polydispersity values (Fig. 5).

The polydispersity of each sample increases with conversion, as anticipated from the increase in branching/-crosslinking. An increase in CTA concentration for fixed concentrations of EGDMA generates products with lower polydispersities (compare series T1 and T2, series T3 and

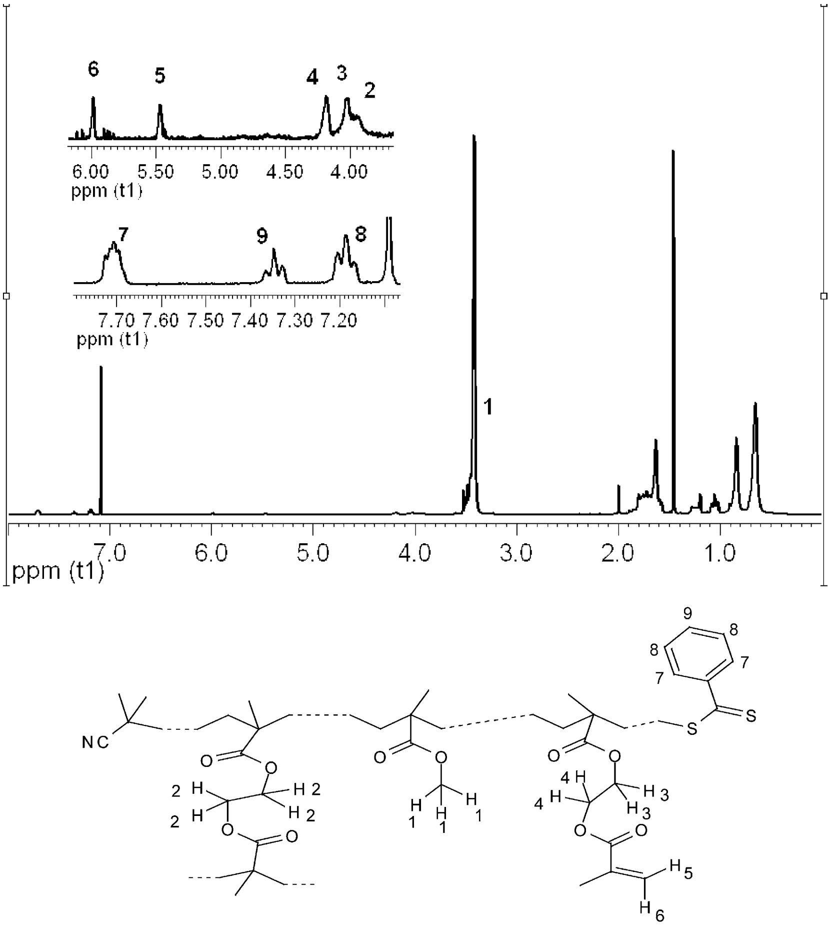

Fig. 1. $^1$H NMR spectrum for a typical poly(MMA-*co*-EGDMA) (31% conversion) synthesized via reversible addition fragmentation chain transfer polymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), mediated by cyanoisopropyl dithiobenzoate [7].

T4), and the lowest ratio EGDMA:CTA (series T2, EGDMA:CTA=0.33) leads to the lowest PDI ($<1.5$ at all temperatures), due to a lower concentration in branching sites (and therefore better control over the molecular weight of linear polymeric chains). From this experiment, it is noteworthy that hyperbranched polymers can be produced that have polydispersities as low as 1.3.

### 3.1. Variations of enthalpy and entropy during RAFT mediated polymerization

The process of a chemical reaction depends on the variation of chemical potential of the reaction system. For a particular component in a polymerization process, e.g. monomer, the relationship between its chemical potential and concentration can be expressed by Eq. (3):

$$\mu = \mu^{\Phi} + RT \ln \frac{C}{C^{\Phi}} \tag{3}$$

$\mu$ and $\mu^{\Phi}$ are the actual chemical potential and standard chemical potential of reacting monomers, respectively, and $C$ and $C^{\Phi}$ are the corresponding monomer concentration. Therefore, a variation in monomer concentration will result in a variation of chemical potential and the final change of chemical potential will follow Eq. (4) at the end of the polymerization:

$$\Delta\mu = RT \ln \frac{C_1}{C_0} = RT \ln(1-x) \tag{4}$$

$C_1$ and $C_0$ are, respectively, the final monomer concentration and the initial monomer concentration, and $x$ is the conversion of monomer. From Eq. (5),

$$\Delta\mu = \Delta\bar{H}_{\mathrm{m}} - T\Delta\bar{S}_{\mathrm{m}} \tag{5}$$

One can deduce Eq. (6):

$$\ln(1-x) = \frac{\Delta\bar{H}_{\mathrm{m}}}{RT} - \frac{\Delta\bar{S}_{\mathrm{m}}}{R} \tag{6}$$

$x$ is the monomer conversion during polymerization. Eq. (6) indicates that the monomer conversion relies intrinsically on the changes in the enthalpy and entropy of the reaction of a molecule of monomer with the propagating radical, and allows quantification of the relationship between the monomer conversion and the temperature. The plot of $\ln(1-x)$ vs. $1/T$ ($\mathrm{K}^{-1}$) permits to verify that a linear relationship is obtained and allows for the quantification of

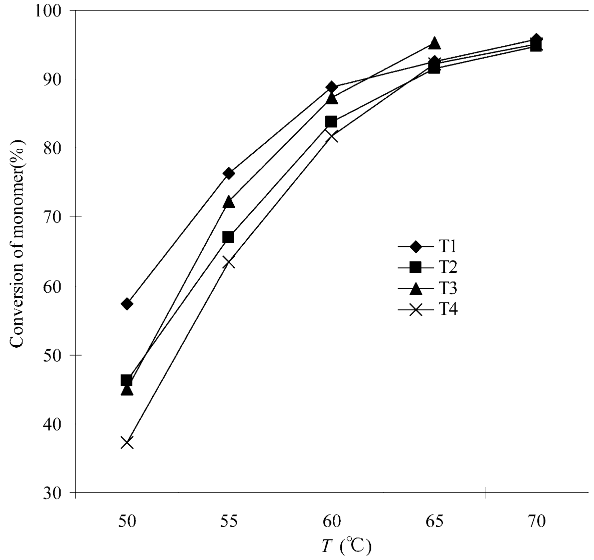

Fig. 2. Monomer conversion for the copolymerization of methyl methacrylate (MMA) and ethylene glycol methacrylate (EGDMA) mediated by chain transfer agent (CTA) cyanoisopropyl dithiobenzoate in presence of azobis (isobutyronitrile) (AIBN), at various reaction temperatures, for series T1 (CTA:MMA:EGDMA:AIBN = 1.00:100:1.00:1), series T2 (CTA:MMA:EGDMA:AIBN = 3.00:100:1.00:1), series T3 (CTA:MMA:EGDMA:AIBN = 3.00:100:5.85:1) and series T4 (CTA:MMA:EGDMA:AIBN = 5.04:100:5.85:1).

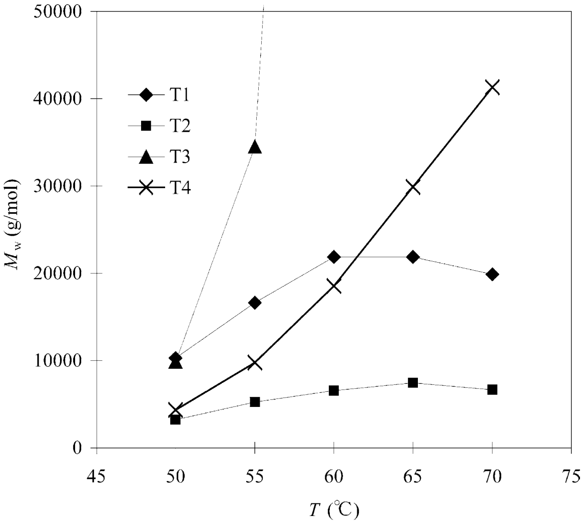

Fig. 4. Variation of $M_w$ with temperature for the copolymerization of methyl methacrylate (MMA) and ethylene glycol methacrylate (EGDMA) mediated by chain transfer agent (CTA) cyanoisopropyl dithiobenzoate in presence of azobis (isobutyronitrile) (AIBN), at various reaction temperatures, for series T1 (CTA:MMA:EGDMA:AIBN = 1.00:100:1.00:1), series T2 (CTA:MMA:EGDMA:AIBN = 3.00:100:1.00:1), series T3 (CTA:MMA:EGDMA:AIBN = 3.00:100:5.85:1) and series T4 (CTA:MMA:EGDMA:AIBN = 5.04:100:5.85:1). Note, for a better clarity of the graph, the data from series T3 at 60 °C ($M_w$ = 179,600 g/mol) and at 65 °C ($M_n$ = 686,360 g/mol) have not been included.

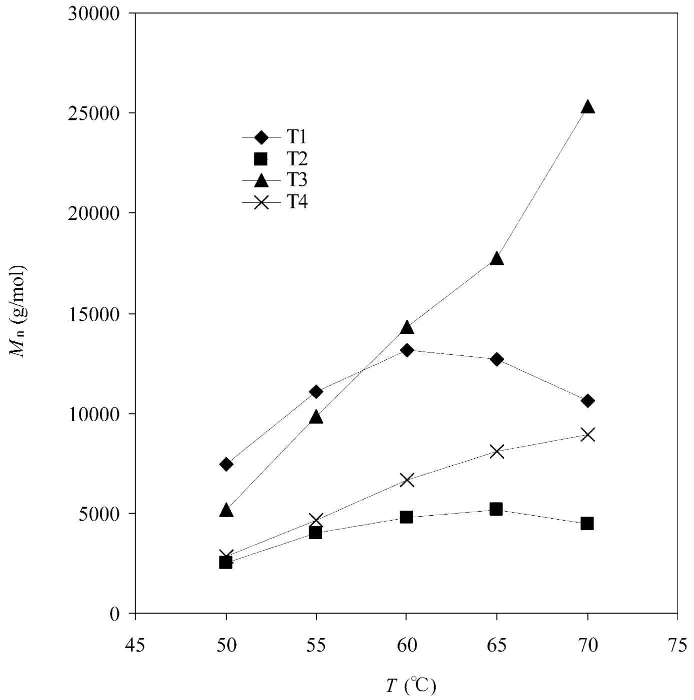

Fig. 3. Variation of $M_n$ with temperature for the copolymerization of methyl methacrylate (MMA) and ethylene glycol methacrylate (EGDMA) mediated by chain transfer agent (CTA) cyanoisopropyl dithiobenzoate in presence of azobis (isobutyronitrile) (AIBN), at various reaction temperatures, for series T1 (CTA:MMA:EGDMA:AIBN = 1.00:100:1.00:1), series T2 (CTA:MMA:EGDMA:AIBN = 3.00:100:1.00:1), series T3 (CTA:MMA:EGDMA:AIBN = 3.00:100:5.85:1) and series T4 (CTA:MMA:EGDMA:AIBN = 5.04:100:5.85:1).

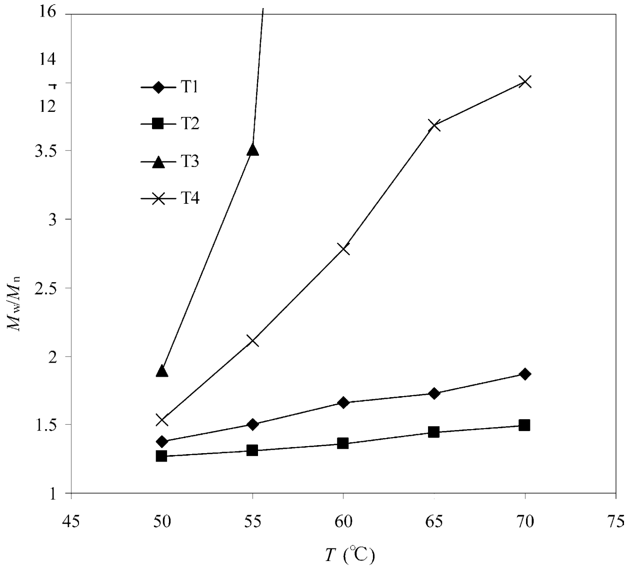

Fig. 5. Variation of the PDI with temperature for the copolymerization of methyl methacrylate (MMA) and ethylene glycol methacrylate (EGDMA) mediated by chain transfer agent (CTA) cyanoisopropyl dithiobenzoate in presence of azobis (isobutyronitrile) (AIBN), at various reaction temperatures, for series T1 (CTA:MMA:EGDMA:AIBN = 1.00:100:1.00:1), series T2 (CTA:MMA:EGDMA:AIBN = 3.00:100:1.00:1), series T3 (CTA:MMA:EGDMA:AIBN = 3.00:100:5.85:1) and series T4 (CTA:MMA:EGDMA:AIBN = 5.04:100:5.85:1). Note, for a better clarity of the graph, the data from series T3 at 60 °C (PDI = 12.5) and at 65 °C (PDI = 27.1) have not been included.

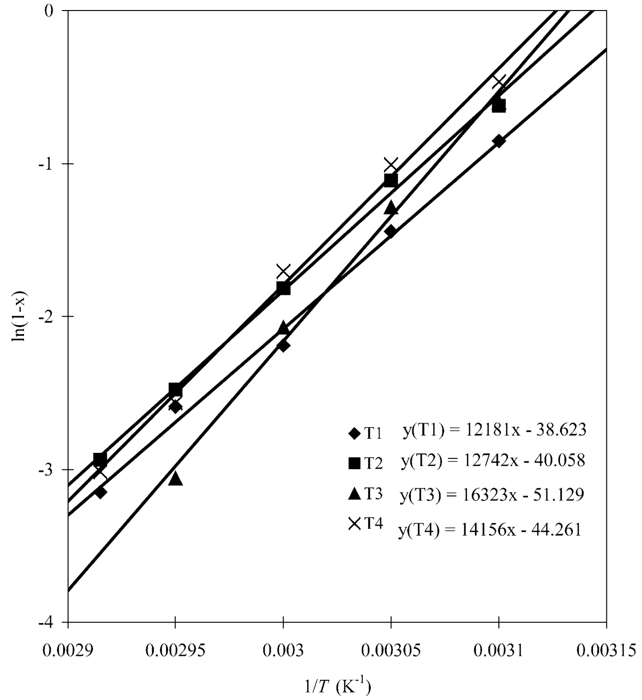

Fig. 6. ln(1 − $x$) vs. 1/$T$ with $x$ = monomer conversion and $T$ = temperature for the copolymerization of methyl methacrylate (MMA) and ethylene glycol methacrylate (EGDMA) mediated by chain transfer agent (CTA) cyanoisopropyl dithiobenzoate in presence of azobis (isobutyronitrile) (AIBN), at various reaction temperatures, for series T1 (CTA:MMA:EGDMA:AIBN = 1.00:100:1.00:1), series T2 (CTA:MMA:EGDMA:AIBN = 3.00:100:1.00:1), series T3 (CTA:MMA:EGDMA:AIBN = 3.00:100:5.85:1) and series T4 (CTA:MMA:EGDMA:AIBN = 5.04:100:5.85:1).

$\Delta\bar{H}_m$ and $\Delta\bar{S}_m$. Fig. 6 shows an excellent agreement of the experimental data with theory. Thus, the variation in the enthalpy and in the entropy can be calculated from the slope and intercept of each plot (Table 2).

The variation of enthalpy $\Delta\bar{H}_m$ indicates the change of the state energy, whereas the variation of entropy ($\Delta\bar{S}_m$) gives a guide to the variation in the degree of order or disorder that is consequent to the polymerization. $\Delta\bar{H}_m$ and $\Delta\bar{S}_m$ represent the variation of partial enthalpy and entropy, respectively, of a monomer molecule, which should not be confused with the overall variation of enthalpy ($\Delta H$) and entropy ($\Delta S$), sum of the partial energies of each constituents of the polymerization system. Typically, for a conventional free radical polymerization of MMA, $\Delta H = -56$ kJ/mol, as quantified by measuring the heat released by the whole reaction system under constant temperature and pressure, and $\Delta S = 112$ kJ/mol [24]. In a RAFT system, $\Delta\bar{H}_m$ and $\Delta\bar{S}_m$ are influenced by more constituents than they would be in a conventional free radical polymerization system (CTA, initiator, the various intermediates of the polymerization, and so on). Therefore the values calculated in this study are only relative to the specific system investigated inhere, and cannot be compared to thermodynamic data of conventional free radical polymerization of MMA. Indeed, the influence of these constituents lead to a positive variation in enthalpy for the monomer reaction, ($\Delta\bar{H}_m > 0$), whilst the overall polymerization reaction is expected to be negative ($\Delta H = -56$ kJ/mol). The

Table 2
Thermodynamic parameters for the copolymerization of methyl methacrylate (MMA) and ethylene glycol methacrylate (EGDMA) mediated by chain transfer agent (CTA) cyanoisopropyl dithiobenzoate in presence of azobis (isobutyronitrile) (AIBN) for series T1 (CTA:MMA:EGDMA:AIBN = 1.00:100:1.00:1), series T2 (CTA:MMA:EGDMA:AIBN = 3.00:100:1.00:1), series T3 (CTA:MMA:EGDMA:AIBN = 3.00:100:5.85:1) and series T4 (CTA:MMA:EGDMA:AIBN = 5.04:100:5.85:1)

| Series | $\Delta\bar{H}_m$ (kJ mol$^{-1}$) | $\Delta\bar{S}_m$ (J mol$^{-1}$ K$^{-1}$) | $\Delta\bar{G}_m$ (J mol$^{-1}$, 60 °C) |
|---|---|---|---|
| T1 | 105.93 | 334.92 | −5600 |
| T2 | 110.76 | 347.61 | −4990 |
| T3 | 151.13 | 472.17 | −6110 |
| T4 | 123.04 | 384.27 | −4923 |

magnitude of the enthalpy variation of the polymerization is shown to depend on both the amount of CTA and brancher (EGDMA). Indeed, when comparing the thermodynamic parameters of series T3 (EGDMA:RAFT = 1.95, $\Delta\bar{H}_m = 151$ kJ mol$^{-1}$ and $\Delta\bar{S}_m = 427$ J mol$^{-1}$ K$^{-1}$) and series T4 (EGDMA:RAFT = 1.16, $\Delta\bar{H}_m =$ 123 kJ mol$^{-1}$ and $\Delta\bar{S}_m = 384$ J mol$^{-1}$ K$^{-1}$), one observes that an increase in the concentration of EGDMA induces an increase in the variation of enthalpy and entropy of the polymerization system. This is an effect of statistics, as EGDMA has two reactive groups and is thus twice as likely to be incorporated as MMA. The increase of entropy encountered in series T3 and T4 can be explained by a lower concentration in CTA, which results in a monomer (MMA) with more orientation opportunities during the polymerization. In the case of series T4, with a concentration in CTA, which is twice as much as that of series T3, the polymerization is strongly retarded, and as expected, both the variations of enthalpy and entropy have lower values than those of T3.

Finally, calculation of $\Delta\bar{G}_m$ at 60 °C for each series confirms the previous observations: series T3 leads to the largest variation in free energy ($\Delta\bar{G}_m = -6110$ J mol$^{-1}$) as it has the highest ratio EGDMA:CTA (= 1.95) by comparison to series T1 ($\Delta\bar{G}_m = -5600$ J mol$^{-1}$, EGDMA:CTA = 1), series T2 ($\Delta\bar{G}_m = -4990$ J mol$^{-1}$, EGDMA:CTA = 1) and series T4 ($\Delta\bar{G}_m = -4923$ J mol$^{-1}$, EGDMA:CTA = 1.16). This is consistent with the observations that the highest concentration in CTA leads to a stronger retardation effect.

## 4. Conclusion

Hyperbranched poly(methyl methacrylate) were synthesized via RAFT polymerization by varying the ratio CTA:MMA:EGDMA:AIBN at 50, 55, 60, 65 and 70 °C. The study demonstrated the controlling effect of the chain transfer agent on the polymerization process, and also indicated the influence of bifunctional monomer on the thermodynamic state of the polymerization process. The rate of polymerization was observed to increase with temperature and concentration in brancher, whilst it was lowered by an increase in chain transfer agent concentration. The molecular weight of the samples increased with the ratios brancher:CTA and monomer:CTA. The polydispersity of the samples increase with conversion, as the level of branching increases. At fixed concentration in brancher, an increase of CTA concentration led to polymers with lower PDI. The variation of enthalpy ($\Delta\bar{H}_m$) and entropy ($\Delta\bar{S}_m$) relative to the monomer reaction were calculated, and it was observed that an increase in the brancher concentration induced an increase in both $\Delta\bar{H}_m$ and $\Delta\bar{S}_m$, whilst lower CTA concentrations led to an increase in $\Delta\bar{S}_m$. The variation in Gibbs energy for the monomer reaction ($\Delta\bar{G}_m$) was calculated at 60 °C, and results confirmed the presence of a retardation effect when increasing CTA concentration generally observed in RAFT polymerization.

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