

Reactivity ratios in conventional and nickel-mediated radical copolymerization of methyl methacrylate and functionalized methacrylate monomers

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Abstract

Copolymerization of an excess of methyl methacrylate (MMA) relative to 2-hydroxyethyl methacrylate (HEMA) was carried out in toluene at 80 °C according to both conventional and controlled Ni-mediated radical polymerizations. Reactivity ratios were derived from the copolymerization kinetics using the Jaacks method for MMA and integrated conversion equation for HEMA ($r_{\text{MMA}} = 0.62 \pm 0.04$; $r_{\text{HEMA}} = 2.03 \pm 0.74$). Poly(ethylene glycol) α -methyl ether, ω -methacrylate (PEGMA, $M_n = 475 \text{ g mol}^{-1}$) was substituted for HEMA in the copolymerization experiments and reactivity ratios were also determined ($r_{\text{MMA}} = 0.75 \pm 0.07$; $r_{\text{PEGMA}} \sim 1.33$). Both the functionalized comonomers were consumed more rapidly than MMA indicating the preferred formation of heterogeneous bottle-brush copolymer structures with bristles constituted by the hydrophilic (macro)monomers. Reactivity ratios for nickel-mediated living radical polymerization were comparable with those obtained by conventional free radical copolymerization. Interactions between functional monomers and the catalyst ($\text{NiBr}_2(\text{PPh}_3)_2$) were observed by ^1H NMR spectroscopy.

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Keywords: Controlled radical polymerization; Nickel-mediated polymerization; Copolymers; Reactivity ratios; Jaacks method; 2-hydroxyethyl methacrylate

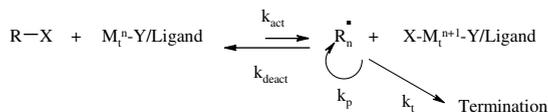
1. Introduction

Transition-metal mediated living radical polymerization reported independently by Sawamoto and coworkers [1] and Matyjaszewski and coworker [2] in 1995 proved to be a remarkably efficient method to produce well-defined macromolecules with a wide range of func-

tionality and architectures [3,4]. This polymerization process is often referred to as atom transfer radical polymerization (ATRP) and in most cases is reported to proceed via a perturbation of a conventional free-radical mechanism, Scheme 1. The process involves a reversible homolytic bond cleavage of a (pseudo)halogen from the initiator or dormant polymer chain. This results in a low steady state, self-regulated concentration of propagating polymer chains that allow slow chain growth whilst minimizing irreversible bimolecular termination. Monomer reactivity ratios and polymer stereochemistry (tacticity)

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Scheme 1. Mechanism of transition-metal mediated living radical polymerization.

are in most cases often similar, but not always identical, to those observed in conventional free-radical polymerizations. Nevertheless, the presence of an additional step (activation/deactivation) and of the metal complex in the reaction medium may be expected to affect the mechanism and ultimately the structure and properties of the resulting polymer. The exact nature of the metallo-organic species is not fully understood under the polymerization conditions. Indeed, under appropriate conditions, significant differences can be observed between conventional free-radical and transition-metal mediated radical polymerizations. For instance, it has been demonstrated that the polarity of the reaction medium substantially influences the polymerization rate, e.g., in aqueous [5] or ethylene carbonate [6] solutions, or through the addition of poly(oxyethylene) derivatives [7] and substituted phenols [8]. It is likely that these differences are due to interactions between these solvents or additives and the catalyst [9], varying the rates of activation and deactivation (k_{act} and k_{deact} in Scheme 1). The possibility that interactions between the monomer and the catalyst can affect the role of the catalyst, and the reactivity of the monomer and/or propagating radicals is of interest. Such an effect is suggested by a recent paper describing the enantioselective transition-metal mediated polymerization of 2,4-pentanedyl dimethacrylate in the presence of a chiral ligand [10].

In the copolymerization of two monomers, A and B, the reactivity ratio, r_A , is defined as the ratio k_{AA}/k_{AB} , where k_{AA} is the rate constant of the reaction between a growing polymer chain having A as its terminal unit and monomer A (homopropagation), and k_{AB} is the rate constant of the reaction between the same reactive chain end and monomer B (cross-propagation). The corresponding reactivity ratio for monomer B, r_B , is defined in the same way. There have been several reports on the determination of reactivity ratios in transition-metal mediated radical copolymerizations, which have generally concluded that the reactivity ratios are very similar to those observed in conventional free radical polymerization [11–13]. Matyjaszewski et al. were the first to report on some discrepancy in the reactivity ratios determined for the copolymerization of methyl methacrylate (MMA) and poly(lactic acid) ω -methacrylate macromonomer between conventional and copper-mediated radical polymerizations [14]. It was attributed to the larger hydrodynamic volume and consequently the smaller diffusion rate of the macromonomer compared

to MMA so that in conventional free radical polymerization, the rapid growth of the polymer chain depletes the local concentration of macromonomer [15]. The much longer lifetime of active chain end-groups associated with the atom transfer radical polymerization allows the macromonomer to diffuse towards the active site, maintaining equality between local and bulk concentrations. More recently, Haddleton and coworkers [16,17] have shown that for a series of aminoethyl methacrylate monomers and a series of poly(ethylene glycol) methacrylate macromonomers of various molar masses, the monomer reactivities towards MMA differ significantly from those observed in conventional free radical polymerizations. This has been attributed to complex formation between the monomer and ligated catalyst.

In previous papers, we reported on the controlled synthesis of poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) copolymers (poly(MMA-*co*-HEMA)) and poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate-*co*-poly(ethylene glycol α -methyl ether, ω -methacrylate) terpolymers (poly(MMA-*co*-HEMA-*co*-PEGMA)) by nickel-mediated radical polymerization and on their use as hydroxyl multi-functionalized precursors for the ring-opening polymerization (ROP) of (di)lactones [18–20]. The combination of these two consecutive polymerization processes allowed accessing well-defined poly(methacrylate)-*g*-poly(aliphatic ester) copolymers of a wide range of molar masses and compositions. Interestingly, not only the poly(methacrylate)-*g*-poly(aliphatic ester) copolymers but also the polymethacrylate copolymer and terpolymer precursors, i.e. poly(MMA-*co*-HEMA) and poly(MMA-*co*-HEMA-*co*-PEGMA), proved to be amphiphilic with high surface tension activity. Such behavior suggested that the comonomers (functionalized or not) were not randomly distributed along the chains but rather characterized by a more blocky-like distribution. In order to shed some light on this point, the aim of this contribution is to determine the reactivity ratios of MMA/2-hydroxyethyl methacrylate (HEMA) and MMA/poly(ethylene glycol) α -methyl ether, ω -methacrylate (PEGMA) comonomers pairs in nickel-mediated radical copolymerization and to compare them to values obtained in conventional radical copolymerization. From the reactivity ratios of these binary systems, the comonomer distribution along both poly(MMA-*co*-HEMA) copolymers, poly(MMA-*co*-HEMA-*co*-PEGMA) terpolymers and their derivatives will be examined.

2. Experimental part

2.1. Materials

$\text{NiBr}_2(\text{PPh}_3)_2$ (99%, from Aldrich), ethyl 2-bromoisobutyrate (EⁱBBr) (98%, from Aldrich), 1,1'-

Table 1

Time dependence of comonomer conversion in the nickel-mediated copolymerization of MMA and HEMA for an initial $[MMA]_0/[HEMA]_0$ molar ratio of 95/5 in toluene at 80 °C ($[MMA]_0/[HEMA]_0/[E^+BBr]_0/[NiBr_2(PPh_3)_2]_0 = 7.71/0.41/33.7 \times 10^{-3}/16.5 \times 10^{-3} \text{ mol L}^{-1}$)

Entry	Time (h)	MMA		HEMA	
		Conversion (%) ^a	$\ln[MMA]_0/[MMA]$	Conversion (%) ^a	$\ln[HEMA]_0/[HEMA]$
1	1	4.5	0.05	10.0	0.11
2	2	20.0	0.22	31.0	0.37
3	3	24.0	0.28	43.0	0.57
4	4	34.0	0.41	49.0	0.66
5	6	65.0	1.05	80.0	1.61

^a As determined using the following equation: conversion of monomer $i = \frac{m_{0i} - F_{wi} \cdot m_p}{m_{0i}}$, where m_{0i} is the initial weight of monomer i in the feed, F_{wi} is the weight fraction of monomer i in the copolymer as determined by ¹H NMR spectroscopy in CDCl₃ from the relative intensity of the methyl ester protons of MMA repeating units at $\delta = 3.60$ ppm and the α -hydroxyl methylene protons of HEMA repeating units at $\delta = 3.85$ ppm, and m_p is the weight of the recovered copolymer as determined by gravimetry.

azobis(cyclohexanecarbonitrile) (98%, from Aldrich), 1-propanethiol (99%, from Aldrich) and heptane (99%, from Devos-François) were used as received. Poly(ethylene glycol) α -methyl ether, ω -methacrylate (PEGMA) ($M_n = 475$, from Aldrich) and methyl methacrylate (MMA) (99%, from Acros) were passed through a column of basic alumina before use. 2-Hydroxyethyl methacrylate (HEMA) (96%, from Acros) was dried over molecular sieves 4 Å and distilled just before use. Toluene (99+%, from Labscan) was dried by refluxing over calcium hydride for at least 48 h and distilled under N₂ atmosphere before use.

2.2. Nickel-mediated radical copolymerization of MMA and HEMA

In a typical nickel-mediated radical copolymerization of MMA and HEMA (Entry 5 in Table 1), NiBr₂(PPh₃)₂ (0.24 g, 0.3 mmol) was introduced in a Schlenk tube and placed under nitrogen atmosphere. MMA (16.0 mL, 149.6 mmol), HEMA (1.0 mL, 8.0 mmol), toluene (2.3 mL) and ethyl 2-bromoisobutyrate (99 μ L, 0.7 mmol) were then added under nitrogen with a syringe. The mixture was deoxygenated by three freeze–pump–thaw cycles after which the Schlenk tube was immersed in thermostated oil bath at 80 °C. After a reaction time of 6 h, the Schlenk tube was rapidly cooled down to ambient temperature and its content was dissolved in THF. The copolymer was then selectively recovered by precipitation from heptane and the conversion was determined gravimetrically after removal of solvent at 80 °C for one night under reduced pressure (overall conv. = 66.1%). In order to remove out the nickel catalyst, the copolymer was dissolved in tetrahydrofuran and passed through a column of basic alumina. The purified copolymer was recovered by precipitation from heptane, filtration and removal of volatiles until constant weight (recovery yield = 88%, $M_{nPMMA} = 21\,600 \text{ g mol}^{-1}$, $M_w/M_n = 1.15$).

2.3. Nickel-mediated radical copolymerization of MMA and PEGMA

In a typical nickel-mediated radical copolymerization of MMA and PEGMA (Entry 5 in Table 4), NiBr₂(PPh₃)₂ (0.69 g, 0.9 mmol) was introduced in a Schlenk tube and placed under nitrogen atmosphere. MMA (10.0 mL, 93.5 mmol), PEGMA (0.46 mL, 0.9 mmol), toluene (13.8 mL) and ethyl 2-bromoisobutyrate (0.14 mL, 0.9 mmol) were then added under nitrogen with a syringe. The mixture was deoxygenated by three freeze–pump–thaw cycles after which the Schlenk tube was immersed in thermostated oil bath at 80 °C. After a reaction time of 8 h, the Schlenk tube was rapidly cooled down to ambient temperature and its content was dissolved in THF. The copolymer was then selectively recovered by precipitation from heptane and the conversion was determined gravimetrically after drying at 80 °C for one night under reduced pressure (overall conv. = 65.6%). In order to remove out the nickel catalyst, the copolymer was dissolved in tetrahydrofuran and passed through a column of basic alumina. The purified copolymer was recovered by precipitation from heptane, filtration and removal of volatiles until constant weight (recovery yield = 90%, $M_{nPMMA} = 16\,100 \text{ g mol}^{-1}$, $M_w/M_n = 1.20$).

2.4. Conventional free radical copolymerization of MMA and HEMA

In a typical free radical copolymerization of MMA and HEMA (Entry 5 in Table 3), MMA (8.0 mL, 74.8 mmol), HEMA (0.5 mL, 4.1 mmol), toluene (1.2 mL), 1-propanethiol (70 μ L, 0.8 mmol) and 1,1'-azobis(cyclohexanecarbonitrile) (0.04 g, 0.2 mmol) were introduced in a Schlenk tube under nitrogen with a syringe. The mixture was deoxygenated by three freeze–pump–thaw cycles after which the Schlenk tube was immersed in thermostated oil bath at 80 °C. After a

reaction time of 3 h, the Schlenk tube was rapidly cooled down to ambient temperature and its content was dissolved in THF. The copolymer was then selectively recovered by precipitation from heptane. The conversion in copolymer was determined gravimetrically after removal of volatiles at 80 °C for one night under reduced pressure (overall conv. = 54.2%, $M_{n\text{PMMA}} = 13\,500\text{ g mol}^{-1}$, $M_w/M_n = 1.69$).

2.5. Characterization

^1H NMR spectra were recorded in deuterated solvents (d^6 -acetone, CDCl_3) at a concentration of 30 mg/0.6 mL using a Bruker Avance 400. Size exclusion chromatography (SEC) of the copolymers were performed in THF/ NET_3 mixture (95/5 in vol.) using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (1 mL min^{-1} flow rate), a PL autoinjector (200 μL loop volume, 1 mg mL^{-1}), a PL-DRI refractive index detector and a set of three columns: a PL gel 5 μm guard column and two PL gel Mixed-C 5 μm columns. Molar masses and molar masses distribution were calculated with reference to narrow poly(methyl methacrylate) standards.

3. Results and discussion

3.1. Reactivity ratios of MMA/HEMA pair in nickel-mediated and conventional radical copolymerizations

Copolymerization of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) was carried out using ethyl 2-bromoisobutyrate (E^iBBr) and $\text{NiBr}_2(\text{PPh}_3)_2$ as initiator and catalyst, respectively, at 80 °C in toluene. Moineau [21] already demonstrated that HEMA can be incorporated in a controlled fashion into poly(methyl methacrylate) chains PMMA, provided

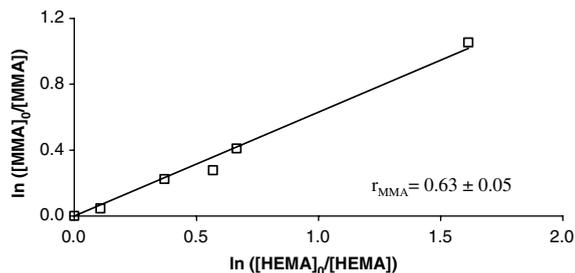


Fig. 1. Jaacks plot of the nickel-mediated radical copolymerization of MMA and HEMA (95:5) as initiated by $\text{E}^i\text{BBr}/\text{NiBr}_2(\text{PPh}_3)_2$ in toluene at 80 °C ($[\text{MMA}]_0/[\text{HEMA}]_0/[\text{E}^i\text{BBr}]_0/[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 7.71/0.41/33.7 \times 10^{-3}/16.5 \times 10^{-3}\text{ mol L}^{-1}$).

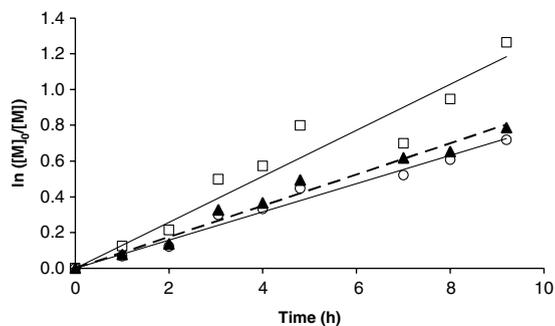


Fig. 2. Kinetic plot of the nickel-mediated copolymerization of MMA and HEMA (88:12) as initiated by $\text{E}^i\text{BBr}/\text{NiBr}_2(\text{PPh}_3)_2$ in toluene at 80 °C ($[\text{MMA}]_0/[\text{HEMA}]_0/[\text{E}^i\text{BBr}]_0/[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 7.15/1.01/3.38 \times 10^{-2}/1.69 \times 10^{-2}\text{ mol L}^{-1}$; $M = \text{MMA}$ (○), HEMA (□), MMA + HEMA (▲)).

that its initial content remains below 20%. Tables 1 and 2 show the time dependence of the comonomer conversions for initial molar fractions in MMA of 0.95 and 0.88, respectively. The Jaacks method [22,23] was preferentially applied since it involves the use of a large excess

Table 2

Time dependence of comonomer conversion in the nickel-mediated copolymerization of MMA and HEMA for an initial $[\text{MMA}]_0/[\text{HEMA}]_0$ molar ratio of 88/12 in toluene at 80 °C ($[\text{MMA}]_0/[\text{HEMA}]_0/[\text{E}^i\text{BBr}]_0/[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 7.15/1.01/3.38 \times 10^{-2}/1.69 \times 10^{-2}\text{ mol L}^{-1}$)

Entry	Time (h)	MMA		HEMA	
		Conversion (%) ^a	$\ln[\text{MMA}]_0/[\text{MMA}]$	Conversion (%) ^a	$\ln[\text{HEMA}]_0/[\text{HEMA}]$
1	1.0	7.0	0.07	12.0	0.12
2	2.0	11.5	0.12	19.0	0.21
3	3.1	26.0	0.30	39.0	0.50
4	4.0	28.0	0.33	44.0	0.57
5	4.8	36.0	0.45	55.0	0.80
6	7.0	39.0	0.50	54.5	0.78
7	8.0	45.5	0.61	61.0	0.95
8	9.2	51.5	0.72	72.0	1.26

^a See legend in Table 1.

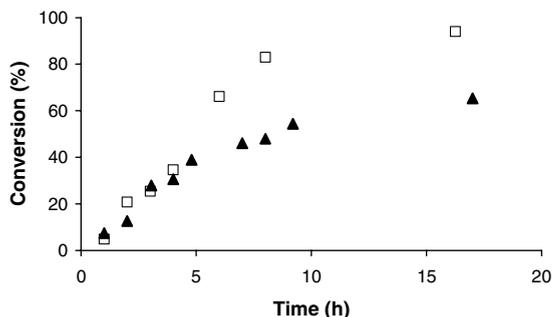


Fig. 3. Time dependence of the global conversion in the copolymerization of MMA and HEMA promoted by E'BBr/ $\text{NiBr}_2(\text{PPh}_3)_2$ in toluene at 80 °C for initial molar fraction in MMA of 0.95 (□, $[\text{MMA}]_0/[\text{HEMA}]_0/[\text{NiBr}_2(\text{PPh}_3)_2]_0/[\text{E}'\text{BBr}]_0 = 7.71/0.41/16.5 \times 10^{-3}/33.7 \times 10^{-3} \text{ mol L}^{-1}$) and 0.88 (▲, $[\text{MMA}]_0/[\text{HEMA}]_0/[\text{NiBr}_2(\text{PPh}_3)_2]_0/[\text{E}'\text{BBr}]_0 = 7.15/1.01/16.9 \times 10^{-3}/33.8 \times 10^{-3} \text{ mol L}^{-1}$).

of one monomer (M_1) relative to the other one (M_2). The reactivity ratio of the monomer in excess is obtained from the linear logarithmic plot of comonomer conversions:

$$r_1 = \frac{\ln \frac{[M_1]_0}{[M_1]}}{\ln \frac{[M_2]_0}{[M_2]}} \quad (1)$$

where $[M_i]_0$, $[M_i]$ are the initial concentration of monomer i and concentration of unreacted monomer i after a given polymerization time, respectively.

The reactivity ratio of MMA (r_{MMA}) calculated from the slope of the plot shown in Fig. 1 is 0.63 ± 0.05 for an initial MMA molar fraction of 0.95. This value is similar to that obtained by Matyjaszewski et al. ($r_{\text{MMA}} = 0.67 \pm 0.02$) for the ATRP copolymerization of MMA and HEMA at 90 °C in xylene (copper-catalyzed ATRP) [13]. Though a single copolymerization experiment might be sufficient to determine r_{MMA} , another copolymerization kinetics was performed from an initial $[\text{MMA}]_0/[\text{HEMA}]_0$ molar ratio of 88/12. In excellent agreement with previous data, r_{MMA} reaches 0.60 ± 0.01 as determined from the slope of the Jaacks plot (not shown here). Fig. 2 shows the linear time dependence of $\ln([M]_0/[M])$ for each comonomer which is consistent with a controlled copolymerization of first order in both MMA and HEMA. Moreover, the polydispersity index remains quite low ($M_w/M_n < 1.4$) whatever the comonomer conversion and the initial molar fraction in MMA. Kinetic data also indicate that HEMA is consumed more rapidly than MMA (Fig. 2) while the global rate of copolymerization for an initial MMA molar fraction (f_{MMA}) of 0.88 is slower than the one for $f_{\text{MMA}} = 0.95$, at least at conversion higher than 40% (Fig. 3). Such a reduction of the copolymerization rate with the HEMA content might be accounted for by specific interactions occurring between HEMA and $\text{NiBr}_2(\text{PPh}_3)_2$ and modifying the catalytic activity of the Ni-based catalyst in the course of the copolymerization. In order to probe such interactions, ^1H NMR spectra of HEMA (a) and a mixture of HEMA and $\text{NiBr}_2(\text{PPh}_3)_2$ (2/1 mol/mol) (b) were recorded in deuterated acetone (Fig. 4). A downfield shift of both α - and

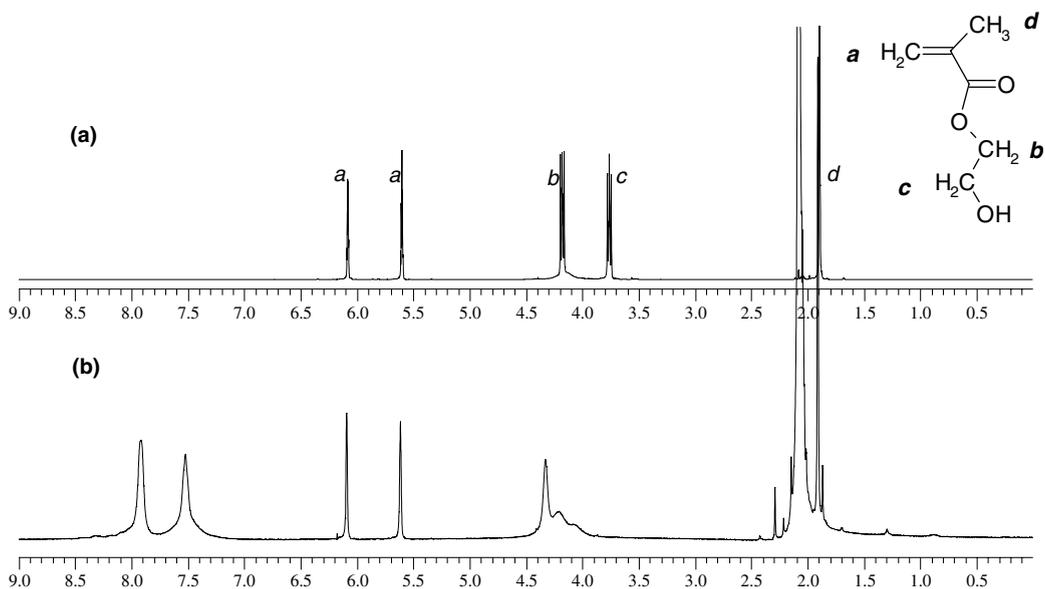


Fig. 4. ^1H NMR spectra (400 MHz) of HEMA (a) and a (2:1) molar mixture of HEMA and $\text{NiBr}_2(\text{PPh}_3)_2$ (b) in deuterated acetone.

β -hydroxyl methylene protons is observed from 3.76 to 4.08 ppm for H_c and from 4.18 to 4.33 ppm for H_b , respectively, together with a broadening of those respective signals. Moreover, it is noted that the initial green solution becomes colorless after a few hours. Such discoloration of the metal complex also occurs by adding coordinating solvents such as methyl alcohol and dimethylsulfoxide while the green colour persists by substituting MMA for HEMA. All of these observations indicate the existence of coordination between the oxygen of the hydroxyl group and the nickel atom.

Based on the r_{MMA} value predetermined by the Jaacks method, the next step consisted in resolving the following integrated conversion equation [24] to approach r_{HEMA} :

$$\text{conversion} = 1 - \left(\frac{f_1}{f_{10}}\right)^\alpha \cdot \left(\frac{f_2}{f_{20}}\right)^\beta \cdot \left(\frac{f_{10} - \delta}{f_1 - \delta}\right)^\gamma \quad (2)$$

where f_{i0} and f_i are the initial and instantaneous molar fractions of monomer i in the feed,

$$\alpha = \frac{r_2}{1 - r_2}, \quad \beta = \frac{r_1}{1 - r_1}, \quad \delta = \frac{1 - r_1 \cdot r_2}{(1 - r_1) \cdot (1 - r_2)},$$

$$\gamma = \frac{1 - r_2}{2 - r_1 - r_2}$$

The best fitting values of r_{MMA} and r_{HEMA} are obtained by minimizing the sum of the squares of the differences between the observed and calculated conversions. Fig. 5 shows the best fit of the integrated conversion equation leading to $r_{\text{MMA}} = 0.62 \pm 0.04$ and $r_{\text{HEMA}} = 2.03 \pm 0.74$. Such reactivity ratios values clearly indicate that the propagating chains will preferably add HEMA over MMA giving rise to poly(MMA-*co*-HEMA) copolymers with a bottle brush-like structure and bristles constituted by HEMA repeating units.

In order to compare reactivity ratios in nickel-mediated and conventional radical copolymerizations, the copolymerization of MMA and HEMA was initiated by 1,1'-azobis(cyclohexanecarbonitrile) (V40) in the presence of 1-propanethiol in toluene at 80 °C for an initial $[\text{MMA}]_0/[\text{HEMA}]_0$ molar ratio of 95/5 (Table 3). As previously observed for nickel-mediated copolymeriza-

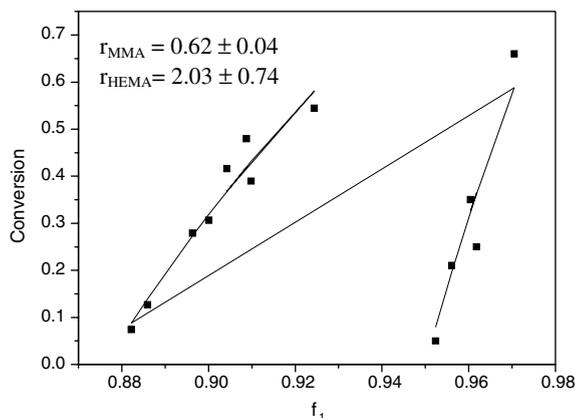


Fig. 5. Plot of the global conversion vs. the instantaneous MMA molar fraction in the feed (f_1). The solid line represents the best fit according to the integrated conversion equation [2].

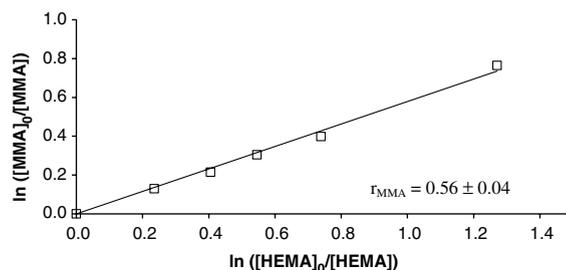


Fig. 6. Jaacks plot of the conventional radical copolymerization of HEMA and MMA (95:5) as initiated by 1,1'-azobis(cyclohexanecarbonitrile) (V40) in the presence of 1-propanethiol in toluene at 80 °C ($[\text{MMA}]_0/[\text{HEMA}]_0/[\text{V40}]_0/[\text{1-propanethiol}]_0 = 7.66/0.42/16.8 \times 10^{-3}/79.1 \times 10^{-3} \text{ mol L}^{-1}$).

tion, the time dependence of comonomer conversions shows that HEMA is consumed more rapidly than MMA. Furthermore, the MMA reactivity ratio as determined by the Jaacks were similar to that obtained by living radical polymerization, i.e. $r_{\text{MMA}} = 0.56 \pm 0.04$ (Fig. 6) compared to $r_{\text{MMA}} = 0.62 \pm 0.04$, respectively.

Table 3

Time dependence of comonomer conversion in the conventional radical copolymerization of MMA and HEMA for an initial $[\text{MMA}]_0/[\text{HEMA}]_0$ molar ratio of 95/5 in toluene at 80 °C ($[\text{MMA}]_0/[\text{HEMA}]_0/[\text{1,1'-azobis(cyclohexanecarbonitrile)}]_0/[\text{1-propanethiol}]_0 = 7.66/0.42/16.8 \times 10^{-3}/79.1 \times 10^{-3} \text{ mol L}^{-1}$)

Entry	Time (h)	MMA		HEMA	
		Conversion (%) ^a	$\ln[\text{MMA}]_0/[\text{MMA}]$	Conversion (%) ^a	$\ln[\text{HEMA}]_0/[\text{HEMA}]$
1	0.5	12.0	0.07	21.0	0.24
2	1.0	19.5	0.12	33.0	0.41
3	1.5	26.0	0.30	42.0	0.55
4	2.0	33.0	0.33	52.0	0.74
5	3.0	53.5	0.45	72.0	1.27

^a See legend in Table 1.

Table 4

Time dependence of comonomer conversion in the nickel-mediated radical copolymerization of MMA and PEGMA for an initial $[\text{MMA}]_0/[\text{PEGMA}]_0$ molar ratio of 99/1 in toluene at 80 °C ($[\text{MMA}]_0/[\text{PEGMA}]_0/[\text{E}^i\text{BBr}]/[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 3.83/0.04/3.79 \times 10^{-2}/3.81 \times 10^{-2} \text{ mol.L}^{-1}$)

Entry	Time (h)	MMA		PEGMA	
		Conversion (%) ^a	$\ln([\text{MMA}]_0/[\text{MMA}])$	Conversion (%)	$\ln([\text{PEGMA}]_0/[\text{PEGMA}])$
1	1.0	2.0	0.02	2.3	0.02
2	2.0	8.6	0.09	11.2	0.12
3	4.0	37.9	0.48	45.1	0.60
4	6.0	53.2	0.76	67.2	1.11
5	8.0	65.1	1.05	75.3	1.40
6	9.9	68.5	1.16	85.8	1.95
7	14.0	72.3	1.28	77.9	1.51

^a As determined using the following equation: conversion of monomer $i = \frac{m_{0i} - F_{wi} m_p}{m_{0i}}$, where m_{0i} is the initial weight of monomer i in the feed, F_{wi} is the weight fraction of monomer i in the copolymer as determined by ¹H NMR spectroscopy in CDCl₃ from the relative intensity of the methyl ester protons of MMA repeating units at $\delta = 3.60$ ppm and the methyl ether group protons of PEGMA repeating units at $\delta = 3.35$ ppm, and m_p is the weight of the recovered copolymer in polymer as determined by gravimetry.

3.2. Reactivity ratios of MMA/PEGMA in nickel-mediated radical copolymerization

The living radical copolymerization of MMA and poly(ethylene glycol) α -methyl, ω -methacrylate (PEGMA, $M_n = 475$) was performed using ethyl 2-bromoisobutyrate (EⁱBBr) and NiBr₂(PPh₃)₂ as initiator and catalyst, respectively, in toluene at 80 °C for an initial molar fraction in MMA of 0.99 (Table 4, initial weight fraction in MMA of 0.95). Since the MMA is in large excess compared to PEGMA, the Jaacks method has been applied to determine the reactivity ratio of MMA (Eq. (1)). As calculated from the slope of the plot in Fig. 7, r_{MMA} reaches 0.75 ± 0.07 . This value is quite similar to that reported previously by Haddleton et al. ($r_{\text{MMA}} = 0.60 \pm 0.05$) for the copper-mediated copolymerization of MMA and PEGMA ($M_n = 475$) at 90 °C in toluene. [16] The same authors have also determined r_{MMA} for the conventional free radical copolymerization

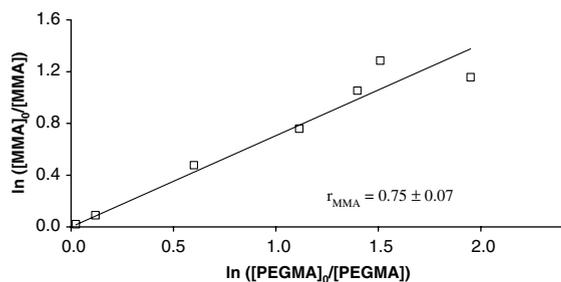


Fig. 7. Jaacks plot of the nickel-mediated radical copolymerization of MMA and PEGMA (99:1) initiated by EⁱBBr/NiBr₂(PPh₃)₂ in toluene at 80 °C ($[\text{MMA}]_0/[\text{PEGMA}]_0/[\text{E}^i\text{BBr}]/[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 3.83/0.04/3.79 \times 10^{-2}/3.81 \times 10^{-2} \text{ mol L}^{-1}$).

and found a value of 0.95 ± 0.03 . When a comonomer M_1 is copolymerized with a much smaller molar ratio

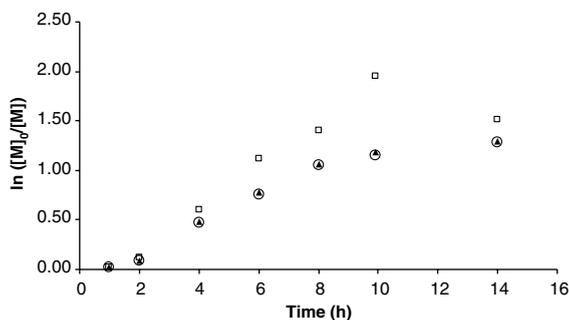


Fig. 8. Kinetic plot of the nickel-mediated radical copolymerization of MMA and PEGMA (99:1) initiated by EⁱBBr/NiBr₂(PPh₃)₂ in toluene at 80 °C ($[\text{MMA}]_0/[\text{PEGMA}]_0/[\text{E}^i\text{BBr}]/[\text{NiBr}_2(\text{PPh}_3)_2]_0 = 3.83/0.04/3.79 \times 10^{-2}/3.81 \times 10^{-2} \text{ mol L}^{-1}$; $M = \text{MMA}$ (○), PEGMA (□), MMA + PEGMA (▲)).

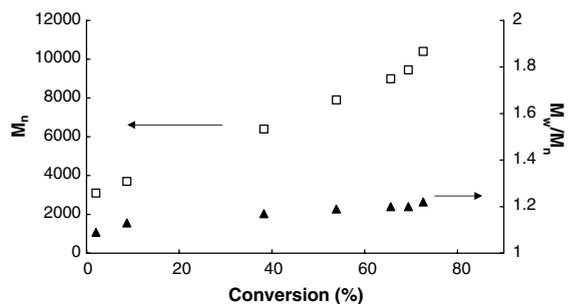


Fig. 9. Dependence of P(MMA-co-PEGMA) macromolecular parameters on global conversion in the copolymerization of MMA and PEGMA initiated with EⁱBBr/NiBr₂(PPh₃)₂ in toluene at 80 °C (apparent M_n (□) and M_w/M_n (▲)).

in macromonomer M_2 , the relative macromonomer reactivity ratio can be approached by $1/r_1$ [25]. In our case, $1/r_{\text{MMA}}$ reaches 1.33 which is consistent with a preferential incorporation of PEGMA over MMA. It might thus be assumed that poly(MMA-*co*-PEGMA) copolymers exhibit a heterogeneous bottle brush-like structure similarly to poly(MMA-*co*-HEMA) copolymers. As shown in Fig. 8, the time dependence of $\ln([M]_0/[M])$, where $[M]_0$ and $[M]$ are the initial and residual global comonomer concentrations, deviates from a linear relationship, at least when MMA conversion exceeds 65–70%. The kinetics also indicates that PEGMA is consumed more rapidly than MMA. Fig. 9 shows the evolution of molecular parameters (apparent number average molar mass of the copolymer (M_n) and polydispersity index (M_w/M_n) vs. global conversion. Apparent M_n increases linearly with the conversion while M_w/M_n remains below 1.25.

4. Conclusion

The binary MMA/HEMA and MMA/PEGMA reactivity ratios for nickel-mediated radical polymerizations were determined using the Jaacks method. We have found that monomers that contain functional groups in the side chain were preferentially incorporated into the copolymers so that bottle brush-like architectures are formed. Thus it can be concluded that previously reported poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate-*co*-poly(ethylene glycol α -methyl ether, ω -methacrylate)) terpolymers (poly(MMA-*co*-HEMA-*co*-PEGMA)) [18–20] adopt a similar architecture with brush bristles constituted by hydrophilic HEMA and PEGMA repeating units. Such a configuration would account for the recently published interfacial tensioactive properties of these terpolymers and those of the related poly(methacrylate)-*g*-[poly(ester)/poly(ether)] graft copolymers [20]. Furthermore, the reactivity ratios were compared with those obtained in conventional free radical copolymerization and found to be similar.

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