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Short communication

A versatile synthesis of poly(lauryl acrylate) using *N*-(*n*-octyl)-2-pyridylmethanimine in copper mediated living radical polymerization

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ABSTRACT

A facile synthesis of poly(lauryl acrylate) has been achieved by atom transfer radical polymerization using benzyl-2-bromoisobutyrate, copper (I) bromide, and *N*-(*n*-octyl)-2-pyridylmethanimine (OPMI). The latter was of great interest as its synthesis was very easy to carry out and as it allowed the reaction mixture to be homogeneous, which was essential for the control of the reaction. The polymerization was controlled under these conditions and was optimized with the addition of copper (II) bromide as deactivator. We proved that the synthesis of poly(lauryl acrylates) with well defined molecular weights and narrow polydispersities was possible using a ligand which does not require difficult synthesis and purification. We also showed the ability of pyridylmethanimine ligands to control ATRP of an acrylate derivative. Best results were obtained at 130 °C in xylene for $[\text{Initiator}]_0/[\text{Cu(I)Br}]_0/[\text{Cu(II)Br}_2]_0/[\text{OPMI}]/[\text{lauryl acrylate}]$ equal to 1/1/0.05/2.2/181, respectively ($M_n = 19{,}942$, DPI = 1.28).

1. Introduction

Polymers derived from long alkyl (meth)acrylates have significant importance in material science. For instance, lauryl (meth)acrylate is of great interest as it can be used for various purposes mainly due to its hydrophobic non polar long pendant alkyl chain that confers high flexibility (low T_g) [1] and side-chain crystallinity properties [2] to the resulting polymer. Poly(lauryl (meth)acrylates) have already been involved in many applications requiring low affinity to water or good swelling properties in the oil [3,4] such as oil absorbency agents [5,6], viscosity modifiers, and oil-soluble drag reducers [7]. To optimize properties and applications of poly(lauryl (meth)acrylate) derivatives, it was essential to produce polymers with well defined structures. Among all possibilities, controlled radical polymerization techniques [8] such as nitroxide-mediated polymerization (NMP) [9,10], reversible addition–fragmentation chain transfer (RAFT) [11,12], and atom transfer radical polymerization (ATRP) [13–16] allowed the synthesis of polymers with well-defined compositions, architectures and functionalities without using such drastic conditions as in ionic methods.

Whereas poly(lauryl methacrylate) has been widely prepared using ATRP [17–21] and RAFT [22] polymerization processes, only a few examples described in the literature the obtaining of poly(lauryl acrylate) (PLAc) using controlled radical polymerization. Coelho et al. described the polymerization of LAc using single-electron transfer/degenerative chain transfer living radical polymerization (SET/DTLRP) in water catalyzed by sodium dithionite [23]. This method allowed the control of the polymerization and permitted to prepare well-tailored lauryl acrylate-based macromolecules in a friendly environmental reaction medium. The atom transfer radical polymerization of lauryl acrylate was also considered and controlled polymerization appeared difficult to achieve. For instance, polymerization reaction performed with CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst using an ionic liquid as the reaction medium [24] showed very significant deviations from controlled

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polymerization conditions as the monomer was poorly soluble in ionic liquid. Reaction performed in a more conventional solvent such as toluene also led to uncontrolled polymerization. Indeed, the poor solubility of the catalyst complex formed with inexpensive multidendate amine ligand PMDETA resulted in poor control of the polymer molecular weights and high polydispersities [25]. The best results were obtained in the presence of copper (II) bromide using the more expensive alkyl substituted bipyridine ligand: 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) with a synthesis particularly difficult to perform. The dNbpy ligand synthesis is quite long as it lasts one week and requires a purification step by distillation using a Kugelrhor apparatus under very high vacuum (10^{-7} Torr) [26].

Herein, we report a controlled polymerization of lauryl acrylate by ATRP using *N*-(*n*-octyl)-2-pyridylmethanimine (OPMI) ligand which was very easy to synthesize and did not require purification step. Polymerization was controlled whatever the molecular weight targeted and was further optimized by adding deactivating copper (II) bromide to the initial reaction mixture. With this contribution, we also show the ability of OPMI to control ATRP of acrylate derivatives.

2. Experimental part

2.1. Materials

Lauryl acrylate (LAc, Aldrich, 90%) was purified by passing through a column of activated neutral aluminum oxide (Al_2O_3 50–200 μm, Acros) to remove inhibitor. Xylene (mixture of isomers, Prolabo) was distilled under reduced pressure. Copper (I) bromide was purified according to the method of Keller and Wycoff [27]. Pyridine-2-carbaldehyde (Acros, 99%), *n*-octylamine (Aldrich, 99%), 2-bromo-2-methylpropionyl bromide (Aldrich, 98%), benzyl alcohol (Avocado, 99%), triethylamine (Prolabo, 99.9%), copper (II) bromide (Aldrich, 99%) and other chemical were used as received.

2.2. General procedures

Polymerizations were carried out using Schlenk line and syringe techniques under nitrogen. Polymer conversions were determined by ^{1}H NMR spectra (δ, ppm) recorded using a Bruker DRX 300 MHz spectrometer. Molecular weight distributions were measured at room temperature using size exclusion chromatography (SEC) with a system equipped with a guard column and HR2, HR3, and HR4 columns (Waters) and a differential refractive-index detector, using tetrahydrofuran at 1 mL min^{-1} as the eluent. Polystyrene standards (Polymer Laboratories) were used to calibrate the SEC (molecular weight range of PS standards: M_p from 1.26×10^3 to 1.92×10^6 g mol^{-1}).

2.3. Synthesis of N-(n-octyl)-2-pyridylmethanimine and benzyl-2-bromoisobutyrate initiator

N-(*n*-Octyl)-2-pyridylmethanimine (OPMI) was synthesized as previously described [28,29] and degassed immediately prior to use. The initiator, chosen to easily determine molecular weights of the resulting polymers by ^{1}H NMR, was synthesized according to known procedure [30].

2.4. Typical atom transfer radical polymerization procedure for lauryl acrylate

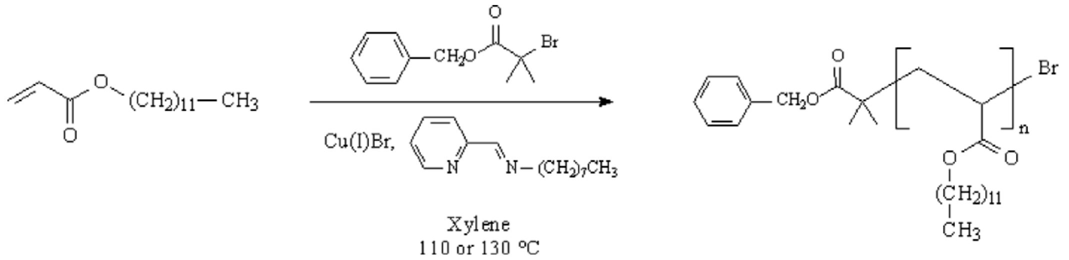
Poly(lauryl acrylate) 5000 (PLAc 5000): copper (I) bromide (87.3 mg, 0.61 mmol), copper (II) bromide (6.8 mg, 0.03 mmol) and benzyl-2-bromoisobutyrate (156.5 mg, 0.61 mmol) were placed in a Schlenk tube under a nitrogen atmosphere. The tube was fitted with a rubber septum and purged five times with nitrogen. Deoxygenated lauryl acrylate (5 mL, 18.1 mmol), and xylene (1 mL) were added using degassed syringes. After four freeze-pump-thaw cycles, the Schlenk tube was immersed in a thermostated oil bath at 130 °C. When the contents reached reaction temperature, OPMI (328 μL, 1.34 mmol) was added via a degassed syringe (time = 0). Samples were taken periodically for conversion and molecular weight analysis. Catalyst residues were removed by passing through a short column of basic alumina using toluene as solvent.

Poly(lauryl acrylate) 15,000 (PAL 15,000): the procedure was the same as polymerization of PAL 5000 described above with the following quantities: copper (I) bromide (58.2 mg, 0.41 mmol), copper (II) bromide (4.5 mg, 0.02 mmol), benzyl-2-bromoisobutyrate (104.3 mg, 0.41 mmol), lauryl acrylate (10 mL, 36.2 mmol), xylene (2 mL), OPMI (219 μL, 0.89 mmol).

Poly(lauryl acrylate) 30,000 (PAL 30,000): the procedure was the same as polymerization of PAL 5000 described above with the following quantities: copper (I) bromide (43.7 mg, 0.3 mmol), copper (II) bromide (3.4 mg, 0.015 mmol), benzyl-2-bromoisobutyrate (78.2 mg, 0.3 mmol), lauryl acrylate (15 mL, 54.3 mmol), xylene (3 mL), OPMI (164 μL, 0.67 mmol).

3. Results and discussion

Initial atom transfer radical polymerization of lauryl acrylate was achieved using copper (I) bromide and *N*-(*n*-octyl)-2-pyridylmethanimine (OPMI) as catalytic system, benzyl-2-bromoisobutyrate as initiator in xylene at 110 °C or 130 °C (Scheme 1). OPMI was used for its facile synthesis and as its long alkyl chain increased compatibility between the catalyst and the monomer, leading to a reaction medium perfectly homogeneous. The *N*-alkyl-2-pyridylmethanimine ligands were developed by Haddleton et al. [31,32] and proved to be very efficient for copper mediated living radical polymerization, mainly for the polymerization of methacrylate or styrene [33] derivatives. On the other hand, these ligands were rarely used for other monomers such as acrylates. Three different molecular weights (5000, 15,000 and 30,000 g mol^{-1}) were targeted at complete monomer conversion (Table 1). All polymerizations gave a linear first-order kinetic plot, indicating that the number of active species remained fairly constant and termination reactions not significant. The molecular weights determined by SEC increased linearly with conver-



Scheme 1. General scheme of the reaction of polymerization of lauryl acrylate using *N*-(*n*-octyl)-2-pyridylmethanimine as ligand and benzyl-2-bromoisobutyrate as initiator.

sion and showed good agreement with theoretical values (Fig. 1) only when low M_n (at high lauryl acrylate conversion) were targeted (PLAc 5000 and 15,000). When higher molecular weights were targeted (especially for PLAc 30,000), a decrease in experimental M_n was observed at high conversion with an increase of PDI to 1.72. This phenomenon could result from transfer reactions particularly favored at 130 °C or from the difference between the reactivity of the initiator compared to the propagating acrylate radical. Final molecular weights determined by ^{1}H NMR (comparison of integrations of the methylene of the benzyl group of the initiator and the methylene in α to the acrylate function of the monomer unit) fitted with theoretical values (Table 1). The polymerization was quite rapid at 130 °C as it was achieved after thirty minutes for poly(lauryl acrylate) 5000 g mol^{-1} (PLAc 5000), whereas ninety minutes were necessary to get PLAc 30,000. The polymerization reaction was also completed at 110 °C for PLAc 5000 to evaluate the influence of the temperature on the control of the polymerization. The evolution of molecular weight versus conversion was linear and a similar polydispersity index (PDI) was obtained, demonstrating that it was useless to work at lower temperature. PDI was quite narrow (Table 1) for both PLAc 5000 and 15,000 (PDI ≈ 1.40) whereas it was relatively high for PLAc 30,000 (PDI = 1.72). Nevertheless, SEC analyses during polymerization showed monomodal peaks whatever the conversion, contrary to what had already been observed in the presence of 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) as ligand, proving that irreversible termination by both coupling and disproportionation occurred at the beginning of the reaction with dNbpy [25].

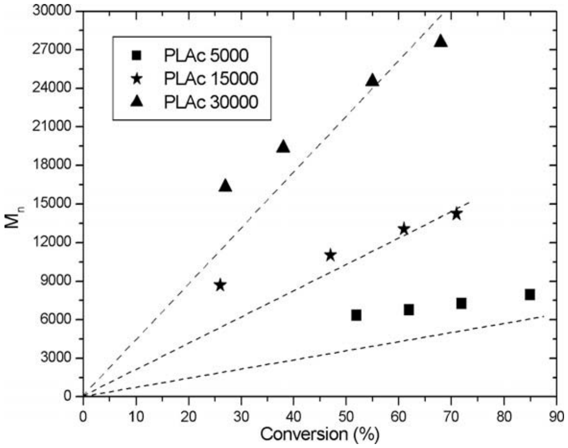


Fig. 1. Molecular weights versus conversion plot for the polymerization of lauryl acrylate in xylene with different molecular weights. [Initiator]/[Cu(I)Br]/[OPMI]/[Monomer] = 1/1/2.2/29.7, 88.2 and 181 for PLAc 5000, 15,000, 30,000 g mol^{-1}, respectively. T = 130 °C. Dash line represents theoretical molecular weight.

From all the experimental results, we concluded that the polymerization was relatively controlled at 130 °C for high molecular weight poly(lauryl acrylate). As a consequence, we tempted to improve experimental conditions studying important factors that could influence the control of the polymerization. To be efficient, an initiating/catalytic system must ensure (1) a relatively fast rate of deactivation compared to the rate of propagation and (2) fast rates of initiation compared to propagation. The proportion of growing radicals should be relatively low to suppress bimolecular termination. The exchange between active and dormant species must also be fast to prepare polymers with low polydispersities. When low rates of deactivation occur, this can be improved by adding a small concentration of Cu(II) halides at the start of the reaction [34]. Using

Table 1
Final conversion and molecular weight data for the polymerization of lauryl acrylate without copper (II) bromide.

Entry	Temp. (°C)	Conv. (%)	Time (min)	$M_{n,th}$[a] (g mol^{-1})	$M_{n,exp}$[b] (g mol^{-1})	$M_{n,exp}$[c] (g mol^{-1})	PDI[b]
PLAc 5000	130	85	30	6053	7940	6120	1.39
PLAc 5000	130	62	15	4415	6767	_	1.39
PLAc 5000	110	60	75	4303	5866	_	1.41
PLAc 15,000	130	71	60	14,551	14,251	14,400	1.40
PLAc 30,000	130	68	90	29,773	27,574	28,634	1.72

[a] $M_{n,th} = ([M]_0/[I]_0 \times M_w$ of monomer $\times$ conv)/100.
[b] Estimated by PS-calibrated SEC.
[c] Estimated by ^{1}H NMR.

Table 2
Final conversion and molecular weight data for the polymerization of lauryl acrylate with copper (II) bromide at 130 °C.

Entry	Conv. (%)	Time (min)	$M_{n,th}$[a] (g mol^{-1})	$M_{n,exp}$[b] (g mol^{-1})	$M_{n,exp}$[c] (g mol^{-1})	PDI[b]
PLAc 5000	82	60	5903	7943	5532	1.37
PLAc 15,000	72	150	15,259	13,637	15,480	1.30
PLAc 30,000	61	480	25,705	19,942	24,840	1.28

[a] $M_{n,th} = ([M]_0/[I]_0 \times M_w$ of monomer $\times$ conv)/100.
[b] Estimated by PS-calibrated SEC.
[c] Estimated by ^{1}H NMR.

more or less Cu(II) deactivator permits to adjust the position of the equilibrium. High concentrations of deactivator accelerate deactivation and reduce polydispersities but also slow down the polymerization.

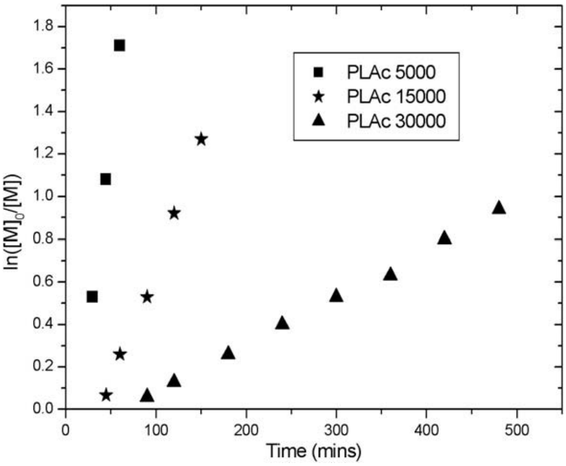


Fig. 2. Kinetics for the polymerization of lauryl acrylate in xylene for different molecular weights. [Initiator]/[Cu(I)Br]/[Cu(II)Br_2]/[OPMI]/[Monomer] = 1/1/0.05/2.2/29.7, 88.2 and 181 for PLAc 5000, 15,000, 30,000 g mol^{-1}, respectively. T = 130 °C.

The polymerization of lauryl acrylate was studied using a small quantity of copper (II) bromide (0.05 mol-% with respect to copper (I) bromide) (Table 2). We first checked that Cu(II) was soluble in the reaction medium at high temperature as a low rate of deactivation is often linked to a poor solubility of the Cu(II) derivative. Kinetic plots of the $\ln([M]_0/[M])$ versus time (Fig. 2) showed good first-order behavior for all molecular weight. As expected, reaction times were longer than without copper (II) bromide and varied from one hour for PLAc 5000 (82% conversion) to eight hours for PLAc 30,000 (61% conversion). The apparent propagation rate constants (k_p^{app}) for the different reactions decreased with increasing molecular weight and were found to be 39×10^{-3}, 11×10^{-3} and 2.2×10^{-3} s^{-1}, for PLAc 5000, 15,000 and 30,000, respectively. We also noticed the presence of an induction period of about 17, 40 and 65 min for the synthesis of poly(lauryl acrylate) 5000, 15,000 and 30,000, respectively which was not observed without Cu(II) deactivator. This induction period was not due to the presence of inhibitor as complete removal of traces of the latter from the monomer was achieved by passing through a column of activated neutral aluminum oxide. Other possibility for the observation of the induction period was the presence of residual molecular oxygen remaining in the reaction mixture. Nevertheless, we assumed that oxygen was completely eliminated as four freeze-thaw cycles were done before polymerization reaction. As a consequence, the induction

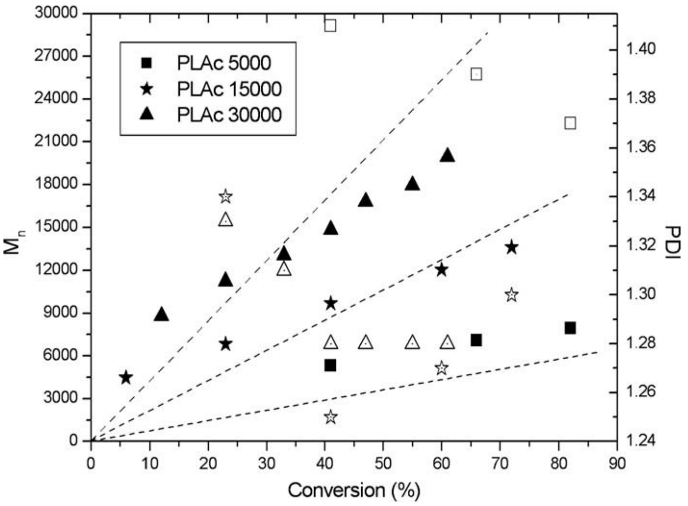


Fig. 3. Molecular weights versus conversion plot for the polymerization of lauryl acrylate in xylene with different molecular weights. [Initiator]/[Cu(I)Br]/[Cu(II)Br_2]/[OPMI]/[Monomer] = 1/1/0.05/2.2/29.7, 88.2 and 181 for PLAc 5000, 15,000, 30,000 g mol^{-1}, respectively. T = 130 °C. Dash line represents theoretical molecular weight. Black and white symbols represent molecular weight (M_n) and polydispersity index (PDI), respectively.

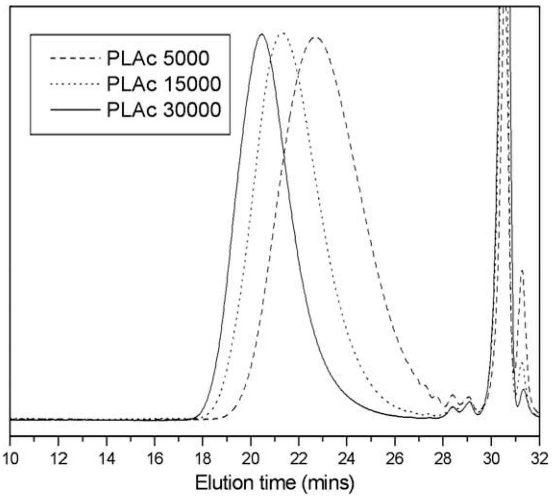


Fig. 4. SEC traces of various PLAc prepared by ATRP in the presence of copper (II) bromide. Polymerization reaction was stopped after 82%, 72%, and 61% conversion for PLAc 5000, 15,000, and 30,000, respectively.

period was attributed to slow establishment of the equilibrium between active and dormant species in the presence of the copper (II) bromide deactivator already mentioned in the literature [35]. As already observed in previous experiments (PLAc 30,000), the molecular weight versus conversion suggests that M_n was higher at the start of the reaction and then fell back to theoretical predictions (Fig. 3). This could be due to initial loss of control early in the reaction due to the highly reactive propagating acrylate, or disparity between both activities of the initiator and of the propagating acrylate radical. Polydispersities appeared to be lower than for reactions without Cu(II) (Table 2). For instance, polydispersity index for PLAc 30,000 after purification was found to be 1.28 whereas it was 1.72 in previous experiment (without copper (II) bromide) and decreased with time. Same kind of results was observed for lower molecular weights. It is also interesting to notice that the best PDI was obtained for the higher molar mass poly(lauryl acrylate). In that case, polymerization reaction went slowly which permitted to optimize the equilibrium between active and dormant species, leading to an excellent experimental result. ^{1}H NMR of the resulting poly(lauryl acrylates) proved that experimental molecular weights were close from theoretical ones. Finally, SEC traces of the resulting polymers (Fig. 4) showed symmetrical and monomodal peaks, confirming the controlled character of the polymerization. Another contribution will show that the produced poly(lauryl acrylates) were used as macroinitiators to reach amphiphilic block copolymers by atom transfer radical polymerization, proving that they possessed a bromide-end atom due to their controlled homopolymerization by ATRP [36].

4. Conclusion

This contribution demonstrated that the atom transfer radical polymerization of lauryl acrylate could be controlled to yield poly(lauryl acrylates) with narrow polydispersities and predetermined molecular weights. The control was achieved by careful selection of the catalytic system and further optimized in the presence of a deactivator. *N*-(*n*-Octyl)-2-pyridylmethanimine was used as ligand for two main reasons: (1) it was easy to prepare and did not need purification step, and (2) it ensured a homogeneous reaction throughout the polymerization. The latter was then optimized using copper (II) bromide as deactivator, leading to a rapid activation–deactivation of the growing chains, allowing the reaction to proceed in a controlled manner irrespective of the target molecular weight. As a consequence, we concluded that *N*-(*n*-octyl)-2-pyridylmethanimine ligand was suitable for the polymerization of acrylate derivatives. In a forthcoming paper, we will use resulting poly(lauryl acrylates) with well defined molecular weights and narrow polydispersities as macroinitiators for the atom transfer radical polymerization of a hydrophilic monomer, leading to amphiphilic macrostructures, whose properties in solution will be reported.

References

[1] Jerome R, Tong JD. Recent developments in anionic polymerization. Curr Opin Solid State Mater Sci 1998;3:573–8.
[2] Hempel E, Huth H, Beiner M. Interrelation between side chain crystallization and dynamic glass transitions in higher poly(*n*-alkyl methacrylate). Thermochim Acta 2003;403:105–14.
[3] Caykara T, Birlik G. Swelling and adsorption properties of hydrophobic poly[(*N*-3-(dimethylamino) propyl) methacrylamide)-co-(lauryl acrylate)] hydrogels in aqueous solutions of surfactants. Macromol Mat Eng 2005;290:869–74.
[4] Waguespack BL, Hodges SA, Bush M, Sondergeld LJ, Bushey MM. Capillary electrochromatography column behavior of butyl and lauryl acrylate porous polymer monoliths. J Chromatogr A 2005;1078:171–80.
[5] Jang J, Kim BS. Studies of crosslinked styrene-alkyl acrylate copolymers for oil absorbency applications. I. Synthesis and characterization. J Appl Polym Sci 2000;77:903–13.
[6] Feng Y, Xiao CF. Research on butyl methacrylate-lauryl methacrylate copolymeric fibers for oil absorbency. J Appl Polym Sci 2006;101:1248–51.
[7] Ma Y, Zheng X, Shi F, Li Y, Sun S. Synthesis of poly(dodecyl methacrylate)s and their drag-reducing properties. J Appl Polym Sci 2003;88:1622–6.
[8] Matyjaszewski K. In: Matyjaszewski K, editor. Controlled/living radical polymerization: From synthesis to materials. Washington, DC: American Chemical Society; 2006.
[9] Hawker CJ. Architectural control in living free-radical polymerizations –preparation of star and graft polymers. Angew Chem Int Ed Engl 1995;34:1456–9.
[10] Farcet C, Charleux B, Pirri R. Poly(*n*-butyl acrylate) homopolymer and poly[*n*-butyl acrylate-*b*-(*n*-butyl acrylate-co-styrene)] block copolymer prepared via nitroxide-mediated living/controlled radical polymerization in miniemulsion. Macromolecules 2001;34:3823–6.
[11] Rizzardo E, Meijs GF, Thang SH. Chain transfer by radical addition–fragmentation mechanisms – synthesis of macromonomers and end-functional oligomers. Macromol Symp 1995;98:101–23.
[12] Barner-Kowollik C. In: Handbook of RAFT polymerization. Wiley VCH; 2008.
[13] Matyjaszewski K, Xia J. Atom transfer radical polymerization. Chem Rev 2001;101:2921–90.
[14] Kamigaito M, Ando T, Sawamoto M. Metal-catalyzed living radical polymerization. Chem Rev 2001;101:3689–745.
[15] Zhang X, Giani O, Monge S, Robin JJ. Synthesis of polypeptide/inorganic hybrid block copolymers. Eur Polym J 2008;44:3676–87.
[16] Monge S, Giani O, Ruiz E, Cavalier M, Robin JJ. A new route for the modification of halogen end groups to amino end-functionalized poly(tert-butyl acrylate)s. Macromol Rapid Commun 2007;28:2272–6.
[17] Xu W, Zhu X, Cheng Z, Chen J. Atom transfer radical polymerization of lauryl methacrylate. J Appl Polym Sci 2003;90:1117–25.
[18] Chatterjee DP, Mandal BM. Facile atom transfer radical homo and block copolymerization of higher alkyl methacrylates at ambient

temperature using CuCl/PMDETA/quaternaryammonium halide catalyst system. Polymer 2006;41:1812–9.

[19] Chatterjee DP, Mandal BM. The ATRP synthesis of the potential thermoplastic elastomer poly(methyl methacrylate)-*b*-(lauryl methacrylate)-*b*-(methyl methacrylate) hitherto unrealized by ionic polymerization. Macromol Symp 2006;240:224–31.

[20] Raghunadh V, Baskaran D, Sivaram S. Efficiency of ligands in atom transfer radical polymerization of lauryl methacrylate and block copolymerization with methyl methacrylate. Polymer 2004;45:3149–55.

[21] Xu Y, Becker H, Yuan J, Burkhardt M, Zhang Y, Walther A, et al. Double-grafted cylindrical brushes: synthesis and characterization of poly(lauryl methacrylate) brushes. Macromol Chem Phys 2007;208:1666–75.

[22] Demetriou M, Krasia-Christoforou T. Synthesis and characterization of well-defined block and statistical copolymers based on lauryl methacrylate and 2-(acetoacetoxy)ethyl methacrylate using RAFT-controlled radical polymerization. J Polym Sci Part A: Polym Chem 2008;46:5442–51.

[23] Coelho JFJ, Carvalho EY, Marques DS, Popov AV, Goncalves PM, Gil MH. Synthesis of poly(lauryl acrylate) by single-electron transfer/degenerative chain transfer living radical polymerization catalyzed by $Na_2S_2O_4$ in water. Macromol Chem Phys 2007;208:1218–27.

[24] Biedron T, Kubisa P. Atom-transfer radical polymerization of acrylates in an ionic liquid. Macromol Rapid Commun 2001;22:1237–42.

[25] Beers KL, Matyjaszewski K. The atom transfer radical polymerization of lauryl acrylate. J Macromol Sci Pure Appl Chem 2001;A38:731–9.

[26] Grimaud T, Matyjaszewski K. Controlled/“living” radical polymerization of methyl methacrylate by atom transfer radical polymerization. Macromolecules 1997;30:2216–8.

[27] Keller RN, Wycoff HD. Copper(I) chloride. Inorg Synth 1947;2:1–4.

[28] Haddleton DM, Crossman MC, Dana BH, Duncalf DJ, Heming AM, Kukulj D, et al. Atom transfer polymerization of methyl methacrylate mediated by alkylpyridylmethanimine type ligands, copper(I) bromide, and alkyl halides in hydrocarbon solution. Macromolecules 1999;32:2110–9.

[29] Haddleton DM, Duncalf DJ, Crossman MC, Jackson SG, Bon SAF, Clark AJ, Shooter AJ. [*N*-Alkyl-(2-pyridyl)methanimine] copper(I) complexes: characterisation and application as catalysts for atom transfer polymerisation. Eur J Inorg Chem 1998:1799–806.

[30] Monge S, Joly-Duhamel C, Boyer C, Robin JJ. Synthesis and characterisation of organogels from ABA triblock copolymers. Macromol Chem Phys 2007;208:262–70.

[31] Haddleton DM. PCT Patent Application WO97/47661, 1997.

[32] Haddleton DM, Jasieczek CB, Hannon MJ, Shooter AJ. Atom transfer radical polymerisation of methyl methacrylate initiated by alkyl bromide and 2-pyridinecarbaldehyde imine copper(I) complexes. Macromolecules 1997;30:2190–3.

[33] Perrier S, Berthier D, Willoughby I, Batt-Coutrot D, Haddleton DM. Living radical polymerization of styrene mediated by copper(I)/*N*-*n*-alkyl-2-pyridylmethanimine ligands 2002;35:2941–8.

[34] Street G, Illsley D, Holder SJ. Optimization of the synthesis of poly(octadecyl acrylate) by atom transfer radical polymerization and the preparation of all comblike amphiphilic diblock copolymers. J Polym Sci A: Polym Chem 2006;43:1129–43.

[35] Even M, Haddleton DM, Kukulj D. Synthesis and characterization of amphiphilic triblock polymers by copper mediated living radical polymerization. Eur Polym J 2003;39:633–9.

[36] Liénafa L, Monge S, Robin JJ, in press.