Hybrid Polymer Particles by Tandem Ring-Opening Metathesis and Atom Transfer Radical Polymerizations in Aqueous Miniemulsion

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Received May 18, 2006
Revised Manuscript Received July 19, 2006

Efforts to replace multistep synthesis by cascade or tandem reactions[1] currently gain momentum, fuelled by the necessity to further maximize synthetic processes and the incorporation of all materials used into the final product. Along this line the concept of concurrent tandem catalysis (CTC) was recently introduced indicating the cooperative action of two or more catalytic reactions in a single reactor.[2] Applied to polymer synthesis, CTC can be used to engineer novel polymeric materials in a reduced number of steps. For instance, linear low-density polyethylene could be successfully synthesized by CTC without adding a comonomer.[3] In a recent addition to this field, block, graft and branched copolymers based on methyl methacrylate (MMA) and ϵ-caprolactone (CL) have been obtained in one-step synthesis by Mecerreyes et al.[4−6] who used various unsymmetrical dual initiators. From the observation made by Noels et al.[7,8] that initiator for ring-opening metathesis polymerization (ROMP) such as $Cl_2(PCy_3)_2Ru{=}CHPh$ can trigger atom transfer radical polymerization (ATRP), Bielawsky et al.[9] designed an unique ruthenium complex that could simultaneously and independently mediate both ROMP and ATRP. Well-defined poly(1,5-cyclooctadiene-*b*-methyl methacrylate) block copolymers were synthesized from this difunctional initiator. This synthetic pathway was adapted later by Novak et al.[10] to prepare graft copolymers by ROMP of cyclobutene derivatives and ATRP of MMA.

Besides these contributions taking advantage of CTC, no publication to our knowledge has addressed the synthesis of hybrid polymer particles using tandem polymerization reactions in dispersed aqueous medium. By hybrid particles we mean particles comprised of two polymers—polynorbornene and poly(methyl methacrylate)—but assembled in different architectures and thus exhibiting different microphase separation/morphologies.

This paper thus investigates the one-pot synthesis of three types of particles obtained through simultaneous ROMP and ATRP carried out in aqueous dispersed medium. Thanks to two new water-soluble macroinitiators (**1**[11] and **2**, Scheme 1) CTC homo- and copolymerizations of MMA and norbornene (NB) could be successfully carried out under miniemulsion conditions.

Two main routes (1 and 2 (parts a and b)) have been explored (Scheme 1). In the first trials (route 1), NB and MMA have been simultaneously homopolymerized in the same particle using **1** as ROMP initiator and ethyl 2-chloroproprionate as ATRP initiator. In subsequent trials (route 2), NB was either copolymerized with **3** and PMMA grown from the initiating sites of **3** or homopolymerized in the presence of **2** whose dangling ATRP initiating sites served to simultaneously grow PMMA branches.

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Prior to these syntheses, preliminary investigations were performed to confirm that **1** and **2** indeed initiate ROMP of NB and the ATRP of MMA, respectively. First, the miniemulsion ROMP of NB initiated by **1** was carried out (experiment 1, Table 1). Then, the miniemulsion ATRP of MMA in the presence of **2** was tried (experiment 2, Table 1). Particles of homopolymers of PNB and PMMA could be isolated in very good yields, with good colloidal stability and rather narrowly distributed molar masses in relatively good agreement with expected values. These results thus attest to the efficiency of **1** and **2** as ROMP and ATRP initiators under miniemulsion conditions.

Next in a typical experiment of hybrid particle's synthesis a miniemulsion was prepared in two step by premixing during 1 h an oily phase consisting of norbornene, methyl methacrylate, hexadecane, ethyl 2-chloroproprionate or **3**, and a water phase containing a polymer surfactant (poly(styrene-*b*-ethylene oxide), PS-*b*-PEO, $M_{n,PS} = 1600$ g/mol; $M_{n,PEO} = 14\,000$ g/mol, PDI $= 1.12$). The macroemulsion obtained was then ultrasonicated at 0 °C for 2 min to get a monomer miniemulsion stable over 20 h. A water solution of **1** or **2** was then introduced into the same reactor at 60 °C triggering the polymerization of the two monomers. The particles obtained under these conditions were characterized and the colloidal properties checked by dynamic light scattering (DLS).

Route 1: The hybrid particles obtained in this way consist of homopolymers of PNB and PMMA generated simultaneously and confined one next to the other in the same compartment (experiment 3, Table 1). The PEO-based ruthenium carbene **1** efficiently serves as ROMP initiator of NB and did not prevent the ATRP from occurring under controlled conditions in the presence of ethyl 2-chloroproprionate. NB was totally consumed in less than 4 h whereas MMA conversion reaches 80% in the same period (Figure 1). The SEC analysis of an aliquot exhibits a bimodal molar mass distribution (Figure 2) with the lower molar mass population corresponding to PMMA chains ($M_w/M_n = 1.18$) and the higher molar mass to PNB chains. The average particle size obtained fits very well with that of the initial droplet confirming that the growth of the two coexisting PNB and PMMA chains occurred under miniemulsion conditions. However, this route induces the formation of about 5% of coagulum with the amount of surfactant used. The latter should be explained by phase separation which occurs between PNB and PMMA chains.

Route 2: The PNB/PMMA particles obtained via this route contain either graft (**4**) or starlike (**5**) copolymers. Particles constituted of PNB-*g*-PMMA (**4**) (route 2a) are generated when a difunctional monomer such as **3** that is capable to propagate ROMP and initiate ATRP of MMA (experiment 4, Table 1) is used in the presence of the ruthenium complex **1** as ROMP initiator and control agent of ATRP. As for particles containing the copolymers **5** (route 2b), they were obtained using the dual initiator **2** (experiment 5, Table 1). The latter can not only initiate the ROMP of NB but can also trigger simultaneously the ATRP of MMA. In both, the conversion of both NB and MMA vs polymerization times was monitored by gas chromatography (GC). The shapes of the MMA and NB conversion curves are relatively similar attesting to the simultaneous consumption of the two monomers (Figure 1) with final conversions close to unity (Table 1). The SEC analysis of an aliquot reveals the formation of only one population of polymer chains indicative

10.1021/ma061118o CCC: $33.50
Published on Web 07/28/2006

Scheme 1. Two Routes Explored to Obtained Hybrid Polymer Particles by Tandem ROM and ATR Polymerizations in Aqueous Phase

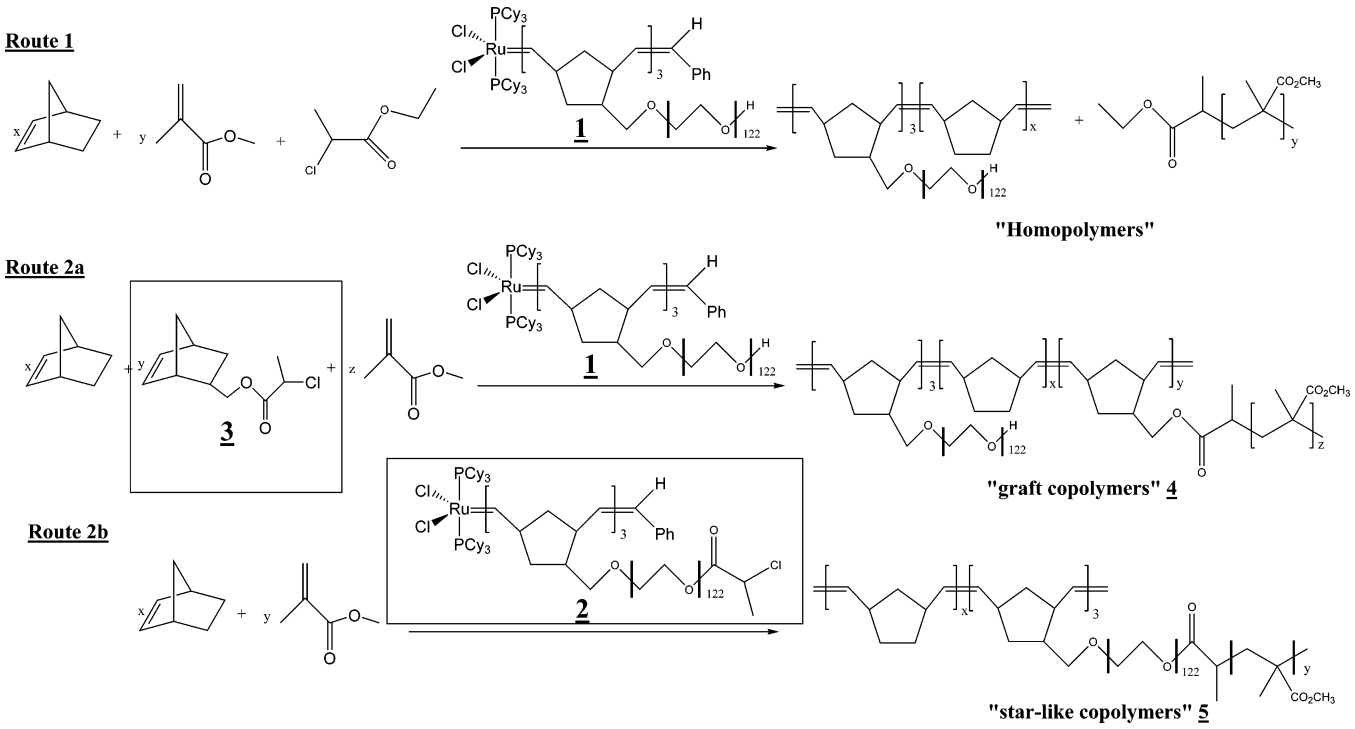

Table 1. Hybrid Particles by Tandem Polymerization of NB and MMA in Aqueous Miniemulsion

expt	polymer	convn$_{MMA}$ [a] (%)	$M_{n,th(PMMA)}$ [b] (g/mol)	$M_{n,expt(PMMA)}$ [c] (g/mol)	M_w/M_n [d]	convn$_{NB}$ [a] (%)	$M_{n,th(PNB)}$ [b] (g/mol)	$M_{n,exp(PNB)}$ [e] (g/mol)	M_w/M_n [d]	D_d (nm) [f]	D_p (nm) [f]
1	PNB					96	93 000	110 000	1.40	216	220
2	PMMA	84	25 000	15 000	1.27					220	224
3	PNB/PMMA	88	26 000	22 000	1.18	99	42 000	130 000	>2	187	194
4	4	87	20 000	*g*	1.36[h]	99	60 000	*g*		148	160
5	5	86	34 000	*g*	1.32[h]	99	62 000	*g*		178	183

[a] Monomer conversions of latices determined by gas chromatography with hexadecane as internal standard. [b] Theoritical values calculated from the initiator-to-monomer ratios taking into account the monomer conversions. [c] Experimental values calculated from size exclusion chromatograms (calibrated by PMMA standards). [d] Determined from size exclusion chromatography. [e] Experimental values from ^{1}H NMR spectroscopy. [f] Droplet and Particle diameters determined by dynamic light scattering. [g] Molar masses of PMMA and PNB could not be dertermined by NMR without error, the PEO signal partially masking the PMMA signal (PEO proton area is the only reference for PNB molar mass calculation). [h] Polydispersity indexes of copolymers.

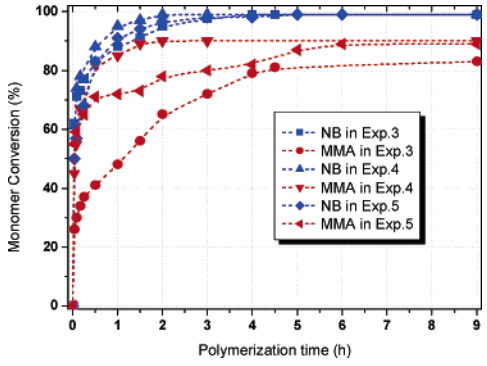

Figure 1. Monomer conversions vs time for tandem miniemulsion polymerization.

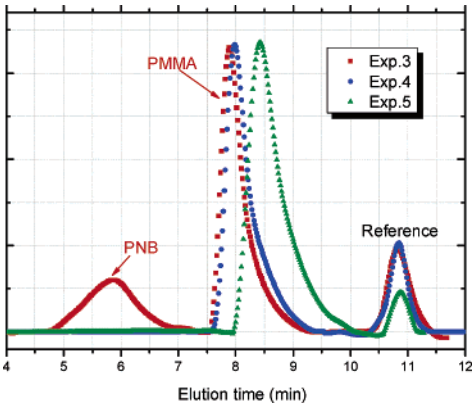

Figure 2. Size exclusion chromatograms of miniemulsion polymerizations: experiment 3, PNB and PMMA homopolymers; experiment 4, graft copolymer **4**; experiment 5, starlike copolymer **5**.

of the formation of the expected copolymer (Figure 2). The resulting polymer particles turn to be perfect one-to-one copies of the initial monomer droplets in size (Table 1). Unlike miniemulsions obtained by route 1, no coagulum was observed in the latter case at the end of the polymerization. These results attest of the very good stability of both the monomer miniemulsions and particles formed.

In brief, we presented in this work novel one step synthesis of hybrid polymer particles in water. Polymerizations of NB by ROMP and of MMA by ATRP could be carried out simultaneously in the presence of purposely designed novel water-soluble ruthenium complexes leading to three types of hybrid particles filled with different architecture (nanoscale blends of homopolymers and graft and starlike copolymers). Investigation are currently undertaken to determine how these architectures impact the microphase morphology with each type of particles and the solid-state proportion of the films formed.

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Supporting Information Available: Text giving details of the preparation and characterization of PEO macromonomer, **1**, **2**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Nicolaou, K. C.; Montagnon, T.; Snyder, S. A. *Chem. Commun.* **2003**, *5*, 551.
(2) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001.
(3) One catalyst oligomerizes ethylene to α-olefins and the second one incorporate these α-olefins into a growing polyethylene chain. Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.
(4) Mecerreyes, D.; Moineau, G.; Dubois, P.; Jérôme, R.; Hedrick, J. L.; Hawker, C. J.; Malström, E. E.; Trollsas, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1274.
(5) Mecerreyes, D.; Atthoff, B.; Boduch, K. A.; Trollsas, M.; Hedrick, J. L. *Macromolecules* **1999**, *32*, 5175.
(6) Mecerreyes, D.; Trollsas, M.; Hedrick, J. L. *Macromolecules* **1999**, *32*, 8753.
(7) Simal, F.; Demonceau, A.; Noels, A. F. Angew. *Chem. Int. Ed.* **1999**, *38*, 538.
(8) Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 5689.
(9) Bielawski, C. W.; Louie, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 12872.
(10) Charvet, R.; Novak, B. M. *Macromolecules* **2004**, *37*, 8808.
(11) Quémener, D.; Héroguez, V.; Gnanou, Y. *J. Polym. Sci.* **2006**, *44*, 2784.

MA061118O