768 *Macromolecules* **2001,** *34,* 768−774

Living Radical Polymerization Immobilized on Wang Resins: Synthesis and Harvest of Narrow Polydispersity Poly(methacrylate)s

Stephanie Angot, Neil Ayres, Stefan A. F. Bon, and David M. Haddleton*

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, U.K.

Received July 6, 2000

ABSTRACT: Wang resin has been transformed into an initiator for copper(I)-mediated living radical polymerization of methacrylates at initiator loading of 0.9 and 3.5 mmol g^{-1}. The immobilized initiator was characterized by ATR FTIR, gel phase ^{13}C NMR, and solid-state CP/MAS ^{13}C NMR using two different spinning frequencies as well as a TOSS pulse sequence. The immobilized initiator has been used to prepare poly(methyl methacrylate), PMMA, homopolymer, and poly(methyl methacrylate)-*block*-poly(benzyl methacrylate-*co*-methyl methacrylate), P(MMA)-*block*-P(BzMA-*co*-MMA), block copolymers. The poly(methacrylate)s have been harvested from the insoluble resin by a simple trifluoroacetic acid, TFA, wash which selectively cleaved the activated benzyl ester linkage, so as to facilitate analysis. At an initiator loading of 0.9 mmol g^{-1} the M_n increases linearly with conversion with kinetics following first-order behavior in monomer as would be expected for living polymerization. After 3 h a 61.9% conversion of MMA is reached, with the isolated polymer chains having an average number molar mass, M_n, of 8200 and a polydispersity, PDI, of 1.18. High conversions, >90%, lead to considerable increases in M_n and PDI. Moreover, small amounts of “free” chains present in the supernatant, ca. 5−8% after 4 h of reaction time, were found. The morphology of the beads was monitored by SEM with the integrity being maintained throughout the transformations. Attempts to prepare true block copolymers via a two-stage process involving isolation of the Wang resins with the first block and subsequent reuse to attach the second block were not satisfactory. However, a one-shot addition of BzMA at high conversion of MMA allowed the synthesis of P(MMA)-*block*-P(BzMA-*co*-MMA) with a narrow molar mass distribution, as confirmed with SEC, DSC, and NMR. The paper demonstrates that Wang immobilized chemistry can be used to prepare excellent polymers maintaining the characteristics of analogous homogeneous living radical polymerizations while allowing for catalyst removal by simple washing procedures. The potential for automation of this chemistry for high throughput synthesis has been demonstrated.

Introduction

Transition-metal-mediated living radical polymerization has been developed as an efficacious technique for the controlled polymerization of (meth)acrylic and styrenic monomers under free-radical-like polymerization conditions.[1−4] A variety of transition metal complexes/ligands has been reported as catalysts for the synthesis of well-defined polymers.[5−11] This chemistry is relatively easy to carry out and very robust with tolerance to most functional groups, which may be present either in reagents or from impurities within the system. These types of polymerizations lead to an unprecedented range of controlled architecture polymers including star polymers,[12−14] block copolymers,[15−17] polymer brushes,[18,19] amphiphilic polymers,[20] glycopolymers,[21] etc. One of the major drawbacks of this chemistry is the high levels of transition metal salt used—often equimolar concentrations are required with respect to initiator—causing reaction solutions to be highly colored, usually necessitating a secondary process for catalyst removal. A number of strategies have been reported to alleviate this problem including immobilization of the catalyst on insoluble supports,[22−24] e.g., silica gel, and the use of fluorous biphase reaction media[25] which allows for efficient separation of the catalyst from the product and for the potential for catalyst recycling.

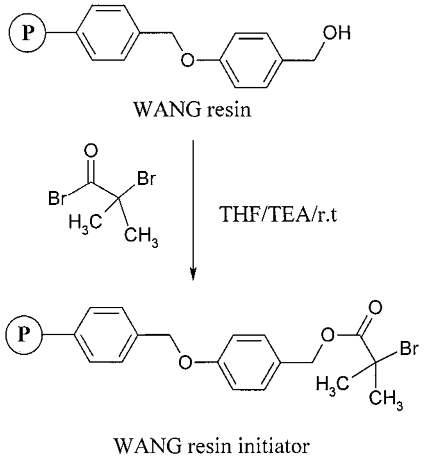
The use of insoluble supports to mediate organic transformations has been developed extensively over recent years. In particular, combinatorial and fast throughput synthesis techniques have become commonplace whereby the organic substrate is transformed while immobilized prior to cleavage and subsequent recovery. This chemistry has grown from the pioneering work of Merrifield[26] with “Merrifield” chloromethyl-functionalized poly(styrene-*co*-divinylbenzene) beads being utilized for more than 20 years for the synthesis of medium-sized peptide using the Boc strategy. The use of a polymeric solid support (resin beads) for organic synthesis relies on three major requirements: (i) a cross-linked insoluble but solvent swellable polymeric material that is inert to the synthesis conditions, (ii) some means of linking the substrate to the solid phase that permit selective cleavage to give the final product, and (iii) a successful synthetic procedure compatible with the linker and the solid phase. One of the most commonly available resins used is Wang resin, which is based on cross-linked polystyrene onto which a 4-hydroxybenzyl alcohol moiety has been attached[27] (Scheme 1). Although solid phase chemistry is now considered almost routine for the synthesis of certain biological polymers (or synthetic polymers with biological activity), the use of insoluble supports has not been extensively developed for synthetic block copolymers. It is noted that Janda has utilized nitroxide-mediated living radical polymerization effectively to prepare soluble polymer supports in a 96 well plate using a combinatorial approach, to give libraries of block and graft copolymers.[28] The advantage of using an insoluble support for metal-mediated polymerization is that it aids the separation of product from catalyst residues by a simple solvent washing procedure.

---

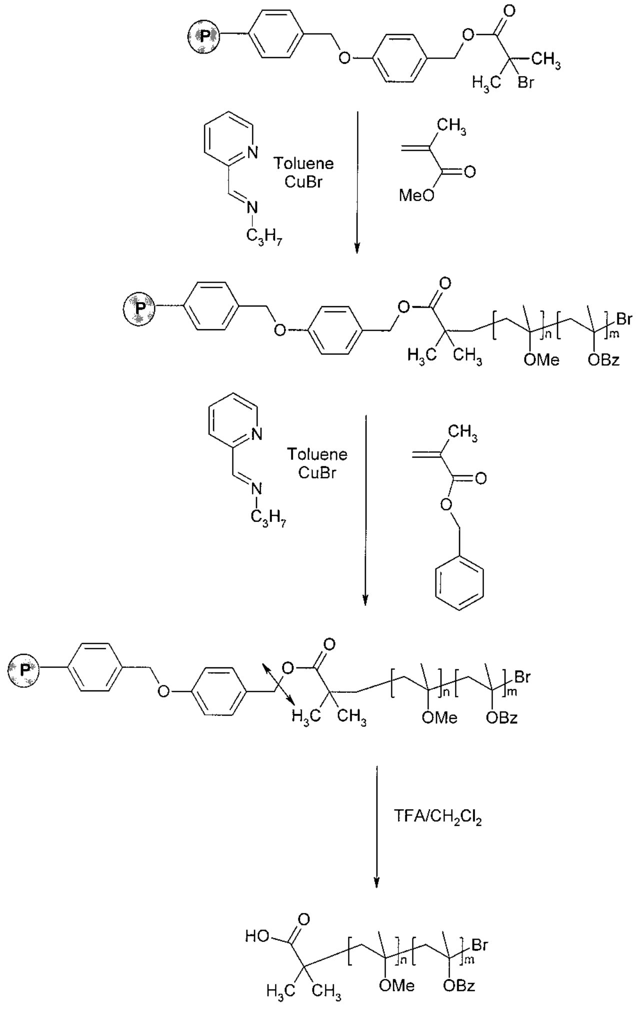
* Corresponding author. E-mail D.M.Haddleton@warwick.ac.uk; phone 44 (0)24 7652 3256; Fax 44 (0)24 7652 4112.

10.1021/ma0011690 CCC: $20.00

Scheme 1. Synthesis of a Solid Supported Initiator on Wang Resin for Transition-Metal-Mediated Living Radical Polymerization



Scheme 2. Synthesis of PMMA-*block*-PBzMA Block Copolymers Using Wang Immobilized Solid Initiator



The development of Wang resin is indeed fortuitous, as we have been developing the transformation of hydroxyl groups into activated alkyl halide based initiators for living radical polymerization for homogeneous reactions.[29] Indeed, a wide range of hydroxyl functional compounds may be condensed with 2-bromoisobutyryl bromide to give functional initiators.[12−14,17] We envisaged that we would be able to combine this approach with the tremendous advances made in resin development for biological polymer synthesis to make polymers with targeted materials properties.

Supported polymer synthesis, as opposed to supported catalysis, e.g., Ziegler−Natta polymerization, is most ideally suited to addition polymerization, which precludes the need for addition, and removal of protecting groups facilitating the synthesis. The main reason for this not being carried out to date is probably that living chain growth polymerization is required and most living polymerization chemistry is not tolerant of most functional groups and/or protic impurities routinely present in solvents and other reagents.[30] Indeed, both nitroxide and transition-metal-mediated living radical polymerization have been utilized to modify suitable surfaces. Hawker has been growing polymer brushes from silicon surfaces[31,32] and Fukuda has used atom transfer radical polymerization on silicon surfaces[18] while Patten has synthesized some interesting nanoparticle hybrids[33] using surface-initiated polymerization. Indeed, Hodges has used TEMPO anchored onto cross-linked polystyrene beads to synthesize “Rasta resins” as novel supports for combinatorial chemistry.[34] However, in all cases to date living radical polymerization from surfaces has always been carried out in order to modify surface properties and not in order to harvest the product as a soluble polymeric product.

It seemed that Wang resins are ideally suited to transformation with functionality suitable for transition-metal-mediated living radical polymerization. This would allow polymers to be grown from the surface of the resin prior to washing out the catalyst/excess monomers and cleavage of the product to harvest relatively pure polymers. The potential for automating this process is also attractive. The main advantage of this approach is the elimination of excess of reagents by simple filtration and solvent washes. The product is isolated by cleavage, under relatively mild conditions, of the activated ester linkage between the resin and the copolymer. This paper reports our initial findings regarding this approach.

Results and Discussion

Initiator Synthesis. Initiator-functionalized resin beads were synthesized from the condensation of Wang resins with a range of hydroxyl loadings (from 1 to 4 mmol g^{-1} of 4-hydroxybenzyl alcohol functionality) and 2-bromoisobutyryl bromide in the presence of triethylamine in tetrahydrofuran suspension at room temperature (Scheme 1). This type of tertiary bromide has been widely used for initiation of living radical polymerization of methacrylates with copper(I) bromide/alkylpyridylmethanimine ligands.[5] ATR FT-IR, gel-phase ^{13}C NMR, and solid state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectroscopy were used to characterize the supported initiator. Acylation of the benzylic hydroxyl group on the resin is observed by the disappearance of the broad hydroxyl stretch, 3450 cm^{-1}, accompanied by the appearance of an intense signal at 1730 cm^{-1} (Figure 1). Excellent gel phase ^{13}C NMR spectra, at 400 MHz, can be obtained by swelling the beads in $CDCl_3$ and collecting spectra under conventional solution NMR conditions. Gel phase NMR shows the presence of the initiator moiety which is more mobile, as compared to the polystyrene core of the beads, with the methyl group, 30.7 ppm, tertiary carbon (−*C*Br), 55.8 ppm, and the ester carbonyl, 171.5 ppm, as would be expected for conventional solution NMR.

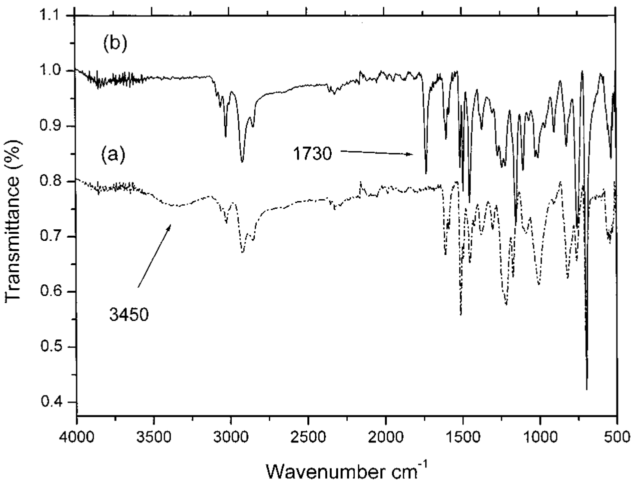


Figure 1. FT-IR spectra of (a) Wang resin and (b) initiator immobilized on Wang resin.

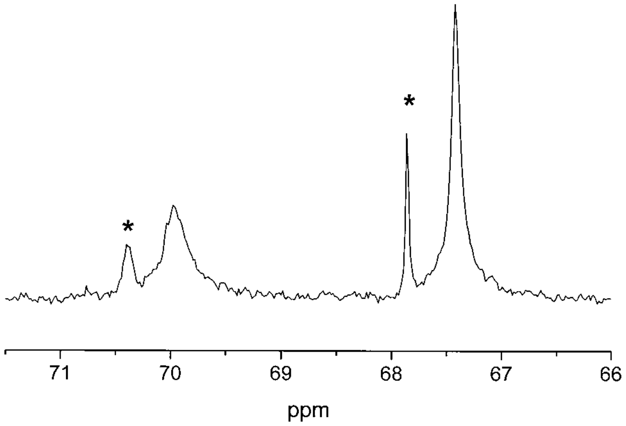


Figure 2. Region of 100 MHz gel phase ^{13}C NMR of Wang initiator showing the benzylic resonances. (*) Unmodified resin.

Figure 2 shows the benzylic resonances of both initiator-functionalized and nonfunctionalized groups. Integration indicates that ca. 87% of the hydroxyl groups have been transformed into initiator sites. ^{13}C CP-MAS solid state NMR study of the resin bound initiator showed the presence of the polystyrene aromatics as a broad peak centered around 120 ppm as well as other characteristic peaks (Figure 3). The CP-MAS spectrum is complicated by spinning sidebands which can be shifted by altering the spinning rate or removed by use of a TOSS (total suppression of spinning sidebands) pulse sequence (Figure 3). The functionalized resin was also characterized by scanning electron microscopy (SEM) showing the spherical nature of the support retained on transformation. The size of the beads is in the range of 150−200 μm as expected according to the data given by the supplier (Figure 4a).

Cleavage of the Polymer Product from the Resin. To monitor polymerization reactions by conventional analytical techniques, it was necessary to cleave the products from the resin support at their point of attachment. The detached polymer chains could be then analyzed using standard techniques such as size exclusion chromatography (SEC) and NMR to obtain molecular weight, polydispersity, and structural information. The attachment via a benzylic ester linkage allows for the cleavage of the polymer products from the resin support by reaction with an excess of trifluoroacetic acid (TFA). This is due to the facile acid cleavage of the Wang attachment promoted by the presence of the trans ether group that stabilizes the formation of the benzylic cationic intermediate. It is noted that the hydrolysis of the backbone ester groups of the polymer, e.g., PMMA, does not occur by this treatment as attested by ^{1}H NMR spectra that confirm the presence of the $-OCH_3$ group, 3.5 ppm, in the final polymers. Moreover, no elimination of HBr at the ω-terminus was observed. Although the cleavage procedure was not optimized, yields of between

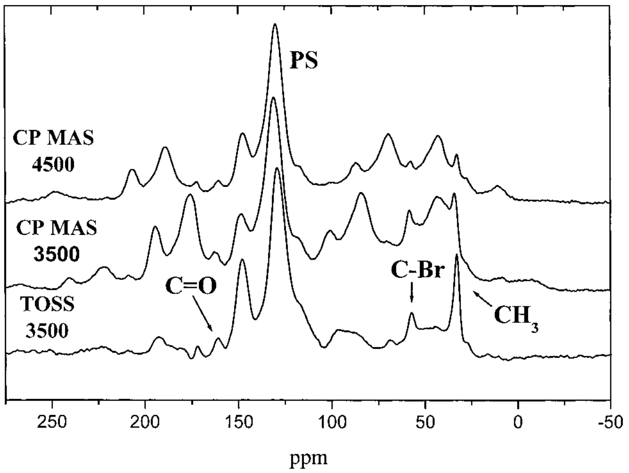


Figure 3. CP MAS solid state ^{13}C NMR immobilized Wang resin initiator. Spectra were recorded at 3500 and 4000 Hz and at 3500 Hz with TOSS pulse sequence.

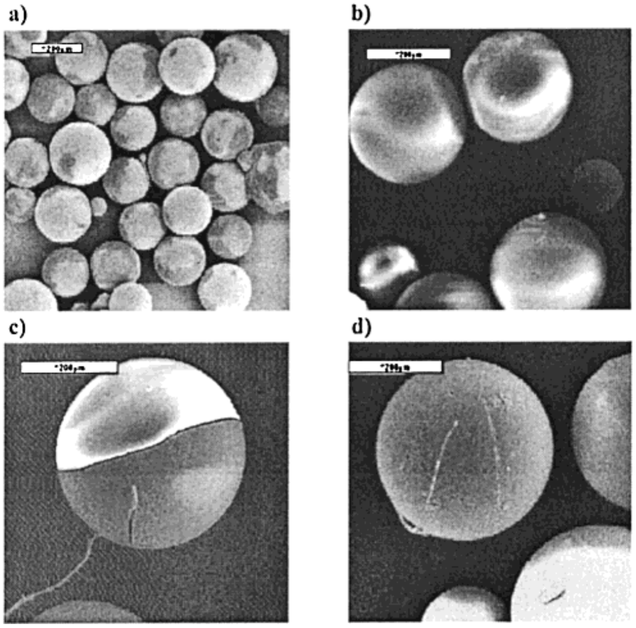


Figure 4. Scanning electron microscopy of (a) Wang resin initiator, (b) PMMA attached to the resin (conversion = 34%), (c) PMMA attached to the resin (conversion = 87.6%), and (d) PMMA-*block*-P(BzMA-*co*-MMA) (run 5). Bar = 200 μm.

Table 1. Data for the Cleavage of Product from 1 g of Recovered Resin

run	recovered polymer (g)	minimum wt % product[a]	yield[b] (%)
8	7.6	88.4	68
4	4.8	82.7	72
7	20.7	95.4	77

[a] Assuming 1 g of recovered material is starting resin. [b] Recovered polymer from gravimetry.

Table 2. Polymerization Data for PMMA Immobilized on Wang Resin; Effect of Initiator Loading and Reaction Concentration on Product Properties

run	init load[a] (mmol g^{-1})	solvent (% v/v)	time (h)	conv[b] (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,exp}$ (g mol^{-1})	PDI
1	3.48	50	3	80	2260	22700	1.80
2	3.48	90	5	10	280	2500	1.32
3	3.48	90	9	15	420	19000	1.30
4	0.87	60	3	61.9	6990	8200	1.18

[a] Estimated from gel phase ^{13}C NMR; see also Figure 2. [b] Obtained by gravimetry.

68% and 77% of recovered soluble polymer were obtained (Table 1). As the cleavage procedure used was designed to avoid hydrolysis of the backbone ester groups, it is anticipated that this has the potential to be improved.

Homopolymers. Polymerization of methyl methacrylate in the presence of Wang resin supported initiator was carried out in toluene solution. The loading of the resin was discovered to be an important parameter governing the molar mass distribution and average molar mass of the final polymer. Two different loadings of resin were utilized to prepare initiators, 3.48 and 0.87 mmol g^{-1} of initiating sites, to investigate this parameter on the overall polymerization behavior. It is noted that supported organic transformations are often carried out at the lower loadings where higher loading can cause complications due to side reactions. Methyl methacrylate was polymerized from the surface of beads with both levels of initiator. Following polymerization, the PMMA was cleaved from the bead with TFA treatment and the product harvested; data for these experiments are given in Table 2. At a loading of 3.48 mmol g^{-1} high conversions are reached at 50% v/v concentration after only 3 h with a loss of control over the number-average molar mass (M_n), $M_{n,exp} = 22\ 700$ g mol^{-1}, whereas its theoretical value is 2260 g mol^{-1} with a relatively high polydispersity (PDI) of 1.80. At higher dilution, 10% v/v monomer, less than 20% conversion is seen after 9 h with PDI remaining approximately 1.30. However, there is still a large discrepancy between targeted and experimental molar masses. A decrease in the loading of the initiator to 0.87 mmol g^{-1} resulted in over 60% conversion being achieved after 3 h. The harvested PMMA showed an excellent PDI of 1.18 and a good agreement between the theoretical, 6990 g mol^{-1}, and experimental molar masses, 8200 g mol^{-1}. Figure 5 shows SEC traces of the final harvested polymers from different loading experiments. At a loading of 3.48 mmol g^{-1} it is envisaged that an increased amount of termination occurs due to the close proximity of the propagating chains which also provides steric constraints for the reaction. A loading of 0.87 mmol g^{-1} leads to excellent products, and thus all further experiments were carried out with 0.87 mmol g^{-1} resins.

Polymerization kinetics were followed in 60% v/v of toluene at 90 °C with at a loading of 0.87 mmol g^{-1}. The M_n of the PMMA increases reasonably linearly with conversion (Figure 6, Table 3), consistently slightly above the theoretical M_n after the initial stages of the reaction, as is often the case with this type of polymerization under homogeneous conditions.[5] The first-order kinetic plot is linear, indicating that the concentration of active centers remains approximately constant throughout the polymerization (Figure 7, Table 3). Under these conditions, the PDI of the product obtained remained less than 1.4, to high conversion. Considerable broadening of the molar mass distribution occurs when the polymerization reaction is proceeded beyond monomer conversions of ca. 80%. At 92.5% conversion the average molar mass deviates further from its theoretical value, 21 400 g mol^{-1} compared to 10 500 g mol^{-1}, and the PDI increases. This is attributed to the increase in viscosity of the reaction medium above approximately 90% conversion, which results in inefficient mixing. The increase in viscosity is due to the consumption of monomer which reduces the amount of liquid present (the monomer represents almost 40% of the liquid phase at the start of the reaction) and also the swelling of the beads in toluene, an excellent solvent for the grafted poly(methacrylate)s. Swelling becomes more important throughout the reaction as the beads become larger,

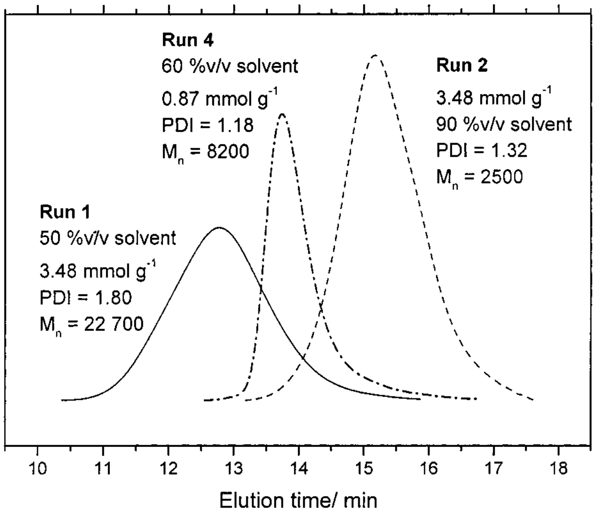


Figure 5. SEC traces of cleaved PMMA products at different initiator loadings at different conversions. See also Table 1.

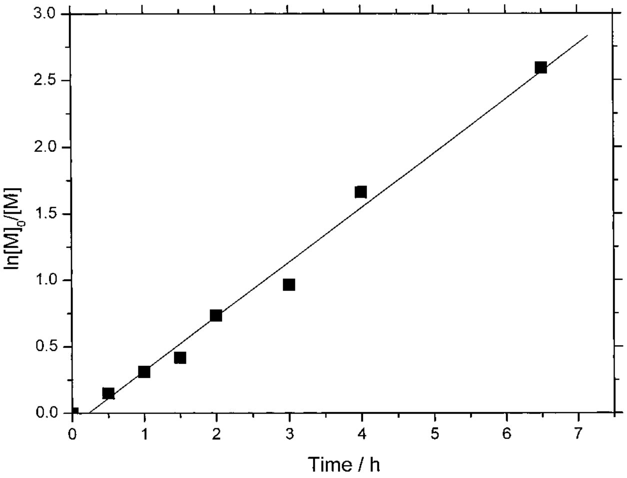


Figure 6. First-order kinetic plot for the solid support polymerization of MMA at 90 °C in the presence of 60% v/v toluene with [M]/[I] = 100. See also Table 2.

Table 3. Synthesis of PMMA by Living Radical Polymerization at 90 °C, 60% v/v Toluene; Evolution of Product Properties with Time

time (h)	conv (%)	$M_{n,th}$[a] (g mol^{-1})	$M_{n,exp}$[b] (g mol^{-1})	PDI
0.5	14	1600	1400	1.33
1	26.7	3000	4600	1.24
1.5	34.2	3900	6000	1.29
2	53.4	6000	7500	1.27
3	61.9	7000	8200	1.18
4	87.6	8600	10700	1.36
6.5[c]	9.25	10500	21400	2.03

[a] Calculated from the [M]/[I] ratio. [b] Obtained by SEC calibrated with MMA standards. [c] Run 8 in Table 1.

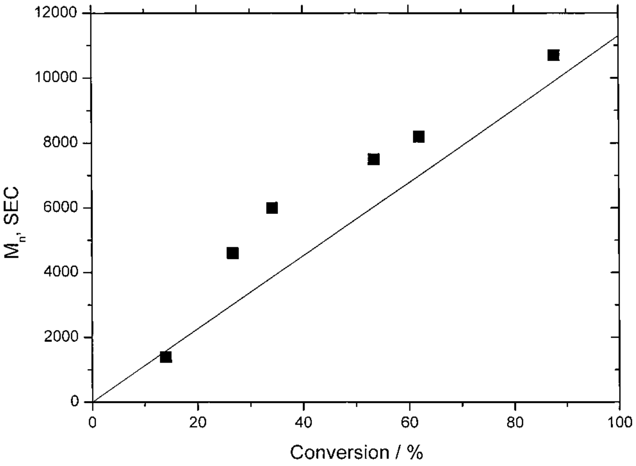


Figure 7. Evolution of M_n with conversion for the solid support polymerization of MMA at 90 °C in the presence of 60% v/v toluene with [M]/[I] = 100. See also Table 2.

resulting in a gelatinous and viscous reaction medium at high conversions. It should be mentioned that NMR analysis of the supernatant of these reactions showed the presence of ca. 5−8% of "free" chains after 4 h polymerization time. The presence of "free" polymer is ascribed to the occurrence of transfer reactions, e.g., to solvent and monomer, to non-covalent-bonded tertiary bromide impurities in the initiator resin (which was indeed observed from ^{13}C gel phase NMR), or to partial cleavage of the polymer chains from the resin during polymerization.

Block Copolymers Synthesis. One of the most useful features of a living polymerization reaction is the ability to synthesize block copolymers. To investigate the potential to prepare immobilized block copolymers, synthesis of PMMA-*block*-PBzMA was attempted by a reinitiation experiment. Poly(methyl methacrylate) as prepared immobilized on the Wang resin was isolated still attached to the resin and combined with a solution of toluene, catalyst solution, and deoxygenated benzyl methacrylate. The mixture was reheated to 90 °C for 8 h. Analysis of the cleaved polymer by 2D SEC (differential refractive index and UV detection) showed a bimodal mass distribution with the presence of the residual PMMA macroinitiator. At present the loss of activity has not been overcome and is ascribed to either termination or deactivation by oxidation during manipulations.

To overcome this difficulty, the second monomer, benzyl methacrylate, was added directly in the reaction medium, without prior isolation of the bead, after approximately 80−90% conversion of MMA, as determined by ^{1}H NMR. This process results in the synthesis of block copolymers where the B block is a statistical copolymer with a maximum amount of 20% of MMA in the B block (Table 4).[35] The SEC trace of this product shows a monomodal, symmetrical peak with a PDI of ca. 1.2. Moreover, the SEC of the block copolymer with both UV and refractive index dual detectors gave identical responses (Figure 8). This indicates regrowth of the PMMA A block to give a copolymer that contains UV-active chromophores from the aromatic benzyl group across the entire mass envelope, excellent evidence of the formation of the block copolymer (Table 4). The average molar masses obtained by SEC analysis are in good accordance with those calculated from the NMR data and the molar mass vs conversion data from Table 4.

Residual Copper in Polymers. The residual copper content in the recovered polymers was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) at Warwick. Two analyses were carried out at different stages of the reaction. First, following recovery of the polymer attached on the resin and washing the reaction medium with appropriate solvents and second after cleavage from the resin and precipitation of the final polymer in methanol. The copper content was 0.039 and 0.001% w/w, respectively, significantly less than the theoretical value of 1.5% w/w if all of the copper from the catalyst remained in the polymer. Thus, the use of the resin supported initiator offers the possibility to easily wash the polymer while immobilized on the resin beads, allowing to reduce the copper level in the final polymers by approximately 97%.

Characterization of Products. Thermal analysis, DSC, of the final block copolymer from experiment 7 gave a single glass transition at 76.8 °C (homopolymers have reported T_g's of 105 and 54 °C for MMA and BzMA, respectively, with the Flory equation predicting a value of 76 °C for this composition ($1/T_g = \omega_a{*}1/T_{g,a} + \omega_b{*}1/T_{g,b}$)). Thus, this indicates formation of a block copolymer where the two blocks are miscible with each other. The miscibility is a result of the low-mass of each block which prevents phase separation.[25] The T_g value increases when the weight fraction of poly(benzyl methacrylate) is decreased to give a single T_g at 81.2 °C (predicted value = 86 °C), experiment 6. ^{1}H NMR also supports a block copolymer (see Supporting Information).

It is important to retain the overall morphology of the resin throughout the reactions. The shape of the resin support and particularly the growth of the polymer around beads were monitored by SEM at different stages of the polymerization. SEM shows an increase in the size of the beads as conversion of MMA increases (Figure 4). For example, the size was measured as 240 μm at 34%, which increases to 370 μm at 87.6% of monomer conversion as compared to 150 μm for the starting resin (Figure 4a−d). These values agree with the theoretical calculated values at each conversion, i.e., 220 and 300 μm, respectively, using values of 0.9569 $cm^3\ g^{-1}$ for the specific volume of the initiator resin and 0.8446 $cm^3\ g^{-1}$ for PMMA (M_n = 10 000). Moreover, the resin support keeps homogeneous in size and distribution all along the polymerization process, which indicates that the beads behave as a reactor for polymerization. This study revealed also that the polymer is covalently attached to the support and growth apart from the solid support initiator.

Table 4. Synthesis of Poly(methyl methacrylate)-*block*-poly(benzyl methacrylate-*co*-methyl methacrylate) at 90 °C in 60% v/v Toluene, Properties of Products

run	conv 1st step[a] (%)	f_{MMA}[b]	total conv (%)	F_{MMA}[c]	$M_{n,emp}$[d] 1st step (g mol^{-1})	$M_{n,th}$[e] (g mol^{-1})	$M_{n,exp}$[f] (g mol^{-1})	$M_{n,exp}$[g] (g mol^{-1})	PDI
5	80	0.17	72.3	0.67	10 100	18 000	24 000	21 000	1.10
6	82.5	0.16	81.1	0.50	10 300	20 200	34 000	35 000	1.20
7	93.4	0.07	89.3	0.46	11 000	22 300	39 000	37 000	1.35

[a] Obtained by NMR, M_n MMA targeted 10 000 g mol^{-1}. [b] Mole fraction of MMA in the monomer feed during the second step, assuming no compositional drift. [c] Cumulative mole fraction of MMA in copolymer obtained by NMR. [d] This empirical value is calculated from the data in Table 2 using the correlation $M_n^2 = -19106628 + 1505589.3 \times \text{conv.}$ [e] Calculated from total conversion (9.36 g of MMA and 15.60 g of BzMA = 100%) and [I]. [f] Obtained by SEC calibrated with MMA standards. [g] Value calculated using $M_n = M_{n,emp} + (M_{n,emp}/MW_{MMA})(1 - F_{MMA})(f_{MMA}MW_{MMA} + 1 - f_{MMA})MW_{BzMA})(F_{MMA} - f_{MMA})$ (see Supporting Information for derivation).

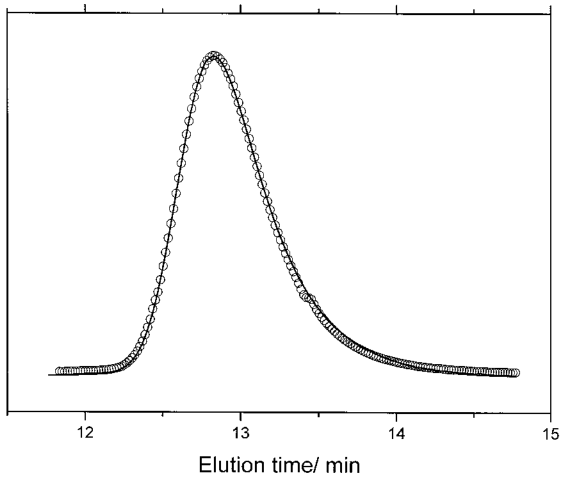


Figure 8. UV (○) and DRI (—) SEC traces of cleaved PMMA-*block*-P(BzMA-*co*-MMA), run 5. See also Table 3.

Summary

Wang resin can be successfully transformed into an effective initiator for copper(I)-mediated living radical polymerization. Polymerization of alkyl methacrylates leads to efficient living polymerization that shows characteristics of living polymerization, including the ability to carry out reinitiation to block/gradient copolymers. An initiator loading of 0.87 mmol g^{-1} results in narrow PDI polymers when the polymerization is carried out at relatively high dilution over a few hours. This allows the product to be isolated from the catalyst and other remainders with simple washing prior to harvesting of the polymer with a simple trifluoroacetic acid (TFA) wash. It is possible to cleave both methyl and benzyl methacrylate polymers without cleavage of the backbone ester groups using this approach. It is envisaged that this will allow for the development of automated rapid throughput synthesis of relatively pure polymers. This is currently under investigation in our laboratory.

Experimental Section

General Information. Methyl methacrylate (MMA) and benzyl methacrylate (BzMA) (Aldrich, 99%) were purified by passing through a column of activated basic alumina so as to remove inhibitor. Copper(I) bromide, triethylamine, 2-bromoisobutyryl bromide, trifluoroacetic acid (Lancaster), toluene (Fisons, 99.8%), and tetrahydrofuran (BDH) were used as received. *N*-(*n*-Propyl)-2-pyridylmethanimine was synthesized as previously described.[5] Avecia Ltd. supplied Wang resin in a range of different loadings (1−4 mmol g^{-1} of OH functionality, size range 150−300 μm).

Prior to polymerization, all solvents, monomers, and other reagents were deoxygenated via a minimum of three freeze−pump−thaw cycles with a rotary pump. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk or syringe techniques.

Synthesis of Wang Resin Initiator. Wang resin, 10 g (1 × 10^{-2} mol, 1 mmol g^{-1} OH functionality), was added to a 250 mL three-necked flask, equipped with a mechanic stirrer. Tetrahydrofuran (150 mL) was added to the flask prior to triethylamine (1.6 mL, 1.1 equiv) and dropwise addition of 2-bromoisobutyryl bromide (1.4 mL, 1.1 equiv). The mixture was slowly stirred with an overhead mechanical stirrer (80 rpm) overnight prior to isolating the supported initiator by filtration. The supported initiator was washed with deionized water with mechanical stirring for 5 h so as to remove triethylammonium salts. The Wang resin supported initiator was recovered by vacuum filtration, and solvents were removed in vacuo. FT-IR (ATR) ν_{max}/cm^{-1}: 1730 ($\nu_{C=O}$) (absence of ν_{OH} at 3100−3500). NMR ^{13}C (CDCl$_3$, 100 MHz, gel phase) δ_{ppm}: 171.5 (*C*=O), 160.0−110.0 aromatic carbons with 159.0 (O−C), 145.1 (q-*C* polystyrene), 114.7 (*o-Ph*O), 70.0 and 67.4 (Ph*C*H$_2$), 55.8 (*C*−Br), 30.7 (*C*H$_3$). Resonances observed at 70.4 and 67.9 (Ph*C*H$_2$) are from nonfunctionalized initiator that was used to calculate a conversion of 87% of the hydroxyl groups to initiator, a loading of approximately 0.87 mmol g^{-1}. Furthermore, a small quantity of nonattached bromide species was observed at 54.9 (*C*Br) and 30.4 (*C*H$_3$).

Homopolymerization Procedure. A typical polymerization was carried out in a 250 mL three-neck flask, equipped with a mechanic stirrer, was added under nitrogen, 1 g of Wang initiator (0.87 mmol g^{-1}, 0.87 × 10^{-3} mol), and 143 mg of CuBr (1.15 equiv, 1 × 10^{-3} mol). A solution of 10 mL of methyl methacrylate (MMA) (M_n = 10 000 g mol^{-1} targeted), 15 mL of anhydrous toluene (60% v/v), and 0.3 mL of *N*-(*n*-propyl)-2-pyridylmethanimine (2.3 equiv, 2 × 10^{-3} mol) was made in a Schlenk tube. Oxygen was removed by three freeze−pump−thaw cycles, and the solution was added to the flask by syringe. The mixture was kept at 90 °C under constant stirring (145 rpm). Following the reaction, the polymerization mixture was cooled to ambient and diluted with tetrahydrofuran. The polymer attached to the resin was recovered by filtration and then washed successively with THF, dichloromethane, and methanol so as to remove excess ligand and copper. The molecular weight of the PMMA was obtained following cleavage under mild conditions of the ester link between the resin and the polymer.

Cleavage Procedure. Immobilized polymer (1 g) was placed in a 100 mL flask with 10 mL of dichloromethane. Trifluoroacetic acid (10 mL) was added dropwise. The mixture was kept under stirring at ambient temperature for 5 h. The dissolved polymer was recovered by filtration, evaporation of the solvent, and precipitation in methanol. NMR ^{1}H (CDCl$_3$, 300 MHz) δ_{ppm}: 0.7−1.1 (CH$_3$), 1.6−2.1 (CH$_2$), 3.6 (OCH$_3$).

Block Copolymerization. (a) Continuous Process/Gradient Copolymer. The first block of PMMA was synthesized as described above. Following reaction at 90 °C (80% conversion of MMA/4 h), 15 mL of benzyl methacrylate (targeted M_n = 10 000 g mol^{-1}) was added under nitrogen flow, and the mixture was stirred at 90 °C. The reaction was subsequently cooled, and the immobilized block copolymer was recovered following washing with THF, dichloromethane, and methanol.

(b) Two-Step Process/Block Copolymer. The first block of PMMA was synthesized as described previously. Following reaction at 90 °C (80% conversion of MMA/4 h), the flask was cooled to ambient temperature. The liquid phase was removed under nitrogen stream with a filter cannula, and the beads were washed four times with deoxygenated toluene. After removal of residual MMA, 143 mg of CuBr was added followed by a degassed solution composed of 15 mL of toluene, 10 mL of benzyl methacrylate, and 0.3 mL of *N*-(*n*-propyl)-2-pyridylmethanimine. The mixture was reheated at 90 °C for a second polymerization. The reaction mixture was subsequently cooled, and the block copolymers were recovered after washing with THF, dichloromethane, and methanol.

Characterization. ^{1}H and ^{13}C solid-state NMR spectroscopy of the compounds attached to the Wang resin were carried out by gel-phase NMR on a Bruker 300 MHz NMR; ^{1}H NMR of the final block copolymer was carried out in $CDCl_3$ solution on a Bruker-DPX 300 MHz spectrometer.

Molecular weight and molecular weight distribution of homopolymers and block copolymers were measured by size exclusion chromatography at ambient temperature on a system equipped with a guard column and two 5 μm mixed D columns (Polymer Laboratories), with both DRI and UV detection, with tetrahydrofuran eluent at 1 mL min^{-1}. Molecular weight was calculated against narrow PMMA standards for DRI and PS standards for UV detection. Polymer conversions were measured by gravimetry. DSC of the final block copolymers was carried out on a Perkin-Elmer Pyris 1. Samples underwent three heating and cooling stages until final measurements was made between 0 and 150 °C at a heating rate of 20 °C min^{-1}.

FTIR spectra of the Wang resin and Wang initiator were recorded on a Bruker VECTOR 22 spectrometer fitted with a golden gate (Specac) attenuated total reflection (ATR) cell. Scanning electron microscopy (SEM) of the resin compounds was carried out on a JEOL JSM-6100. Residual copper analysis was determined using a Leeman Labs inductively coupled plasma atomic emission spectrophotometer (ICP-AES) calibrated with Leeman Labs ICP standards.

Acknowledgment. The authors thank EPSRC for funding (GR/M74245, S.A.; GR/L59224, S.A.F.B.), Dr. S. Pascual for help with SEM, Dr. D. Pears and Dr. A. J. Shooter (Avecia) for helpful discussions and supply of Wang resin. Dr. M. E. Smith and I. J. F. Poplett are thanked for help with solid state NMR.

Supporting Information Available: ^{1}H NMR of final copolymer PMMA-*block*-P(Bz-*co*-MMA) and derivation of the equation to calculate average number molar mass of poly(MMA-*b*-(MMA-*co*-BzMA) grown of modified Wang resin. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(2) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(3) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *32*, 371.
(4) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895.
(5) Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. M.; Kukulj, D.; Shooter, A. J. *Macromolecules* **1999**, *32*, 2110.
(6) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190.
(7) Granel, C.; Teyssie, P.; DuBois, P.; Jerome, P. *Macromolecules* **1996**, *29*, 8576.
(8) Moineau, G.; Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1998**, *31*, 542.
(9) Uegaki, H.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3003.
(10) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. Y. *Macromolecules* **1996**, *29*, 3665.
(11) Percec, V.; Barboiu, B.; Kim, H.-J. *J. Am. Chem. Soc.* **1998**, *120*, 305.
(12) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218.
(13) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762.
(14) Haddleton, D. M.; Edmonds, R.; Heming, A. M.; Kelly, E. J.; Kukulj, D. *New J. Chem.* **1999**, *23*, 477.
(15) Matyjaszewski, K. *Chem. Eur. J.* **1999**, *5*, 3095.
(16) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 5582.
(17) Jankova, K.; Chen, X. Y.; Kops, J.; Batsberg, W. *Macromolecules* **1998**, *31*, 538.
(18) Ejaz, M.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2000**, *33*, 2870.
(19) Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424.
(20) Wang, X.-S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. *Chem. Commun.* **1999**, 1817.
(21) Ohno, K.; Tsujii, Y.; Fukuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2473.
(22) Haddleton, D. M.; Duncalf, D. J.; Kukulj, D.; Radigue, A. P. *Macromolecules* **1999**, *32*, 4789.
(23) Haddleton, D. M.; Kukulj, D.; Radigue, A. P. *Chem. Commun.* **1999**, 99.
(24) Kickelbick, G.; Paik, H. J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*.
(25) Haddleton, D. M.; Jackson, S. G.; Bon, S. A. F. *J. Am. Chem. Soc.* **2000**, *122*, 1542.
(26) Merrifield, R. B. *J. Am. Chem. Soc.* **1966**, *85*, 2149.
(27) Wang, S.-S. *J. Am. Chem. Soc.* **1973**, *95*, 1328.
(28) Gravert, D. J.; Datta, A.; Wentworth, P.; Janda, K. D. *J. Am. Chem. Soc.* **1998**, *120*, 9481.
(29) Haddleton, D. M.; Waterson, C. *Macromolecules* **1999**, *32*, 8732.
(30) Webster, O. W. *Science* **1991**, *Feb*, 887.
(31) Husemann, M.; Morrison, M.; Benoit, D.; Frommer, K. J.; Mate, C. M.; Hinsberg, W. D.; Hedrick, J. L.; Hawker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 1844.
(32) Shah, R. R.; Merreceyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules*, **2000**, *33*, 597.
(33) vonWerne, T.; Patten, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 7409.
(34) Hodges, J. C.; Harikrishnan, L. S.; AultJustus, S. *J. Comb. Chem.* **2000**, *2*, 80.
(35) Matyjaszewski, K. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1785.
(36) Kotani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 6979.

MA0011690