Synthesis of Acrylate and Methacrylate Block Copolymers Using Atom Transfer Radical Polymerization

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ABSTRACT: The synthesis of di- and triblock copolymers, involving methyl methacrylate (MMA), butyl acrylate, and methyl acrylate, using copper-based atom transfer radical polymerization (ATRP) is reported. It was found that poly(MMA) macroinitiator is able to initiate the ATRP of acrylic monomers. However, for polyacrylates to effectively initiate the ATRP of MMA, the end group should be a bromine atom and the catalyst CuCl; that is, halogen exchange should take place. ABA-type triblock copolymers, where B = poly(butyl acrylate) and A = poly(methyl methacrylate), were synthesized by growing the center block first using a difunctional initiator and then adding MMA to the ends.

Introduction

The synthesis of block copolymers is often difficult or impossible in conventional free radical polymerization because the required functionality control is limited.[1] This has resulted in the use of ionic polymerization methods, sometimes combined with free radical polymerization, to synthesize block copolymers. However, the conditions required for such syntheses limit the range of monomers and functionality that can be utilized. In recent times, controlled/"living" free radical polymerization techniques have allowed for the synthesis of polymers with functionality through a radical mechanism that requires less stringent conditions than ionic methods.[2] Furthermore, functionality is introduced into the polymer chain, molecular weights can be predetermined by the concentrations of the initiator and monomer, and polydispersities are often narrow ($M_w/M_n < 1.5$, where M_n and M_w are the number- and weight-average molecular weights, respectively).

Of the several controlled/"living" free radical polymerization techniques,[2] atom transfer radical polymerization (ATRP) seems the most versatile, being able to polymerize a variety of monomers.[3−11] Thus, block copolymers containing quite different monomers may be synthesized through the one technique and potentially in a one-pot reaction. However, several factors still need to be optimized in order for the polymerization to be controlled. It has been shown that the polymerization of MMA using ATRP is not so straightforward; in particular, one needs to ensure that efficient initiation takes place (i.e., initiation is fast).[12,13] To increase the rate of initiation relative to the rate of propagation, "halide exchange" can be utilized. Here, an alkyl bromide initiator is used in conjunction with copper chloride. The result is that the Br group initially provides fast initiation, but thereafter the end group of the growing polymer chain is predominantly the less labile Cl; hence, the rate of initiation is increased relative to the propagation rate, thereby improving initiation efficiency.[14]

Block copolymers of acrylates and methacrylates are not only challenging synthetically but also interesting because of the morphological, phase, and mechanical properties of such polymers. These properties are realized partly through the combination of a high T_g block (methacrylate) with a softer, lower T_g block (acrylate). Furthermore, ABA-type triblock copolymers, where the A-blocks are methacrylates and the B-block is an acrylate, can function as thermoplastic elastomers or specialty adhesives. Such materials are expected to resist hydrocarbon solvents to a greater degree than styrene−butadiene analogues.

In this paper we report the synthesis of block copolymers of methyl methacrylate (MMA) with either *n*-butyl acrylate (BA) or methyl acrylate (MA) by ATRP, paying particular attention to the functionality and the initiation efficiency of the macroinitiator.

Results and Discussion

The general mechanism of ATRP involves the abstraction of a halogen from the dormant chain by a metal center (such as complexes of Cu^I) in a redox process.[2] Upon halogen abstraction, the free-radical formed (the active species) can undergo propagation as in conventional free radical polymerization. However, the free radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the equilibrium that is established favors the dormant species. Because of this, two requirements for a controlled/"living" system are fulfilled.[15] First, all chains can begin growth at (essentially) the same time, and second, the actual concentration of free radicals is quite low, resulting in a markedly reduced amount of irreversible radical−radical termination, especially when relatively low molecular weights are targeted. The final result is that degrees of polymerization (DP) can be predetermined ($DP = \Delta[M]/[I]_0$) and M_w/M_n may be quite low (<1.1). Moreover, the polymer chains contain an active halogen end group, so that the polymer chain can undergo further extension, either with the monomer used in its synthesis or with a second monomer, therefore forming a block copolymer.

Tables 1 and 2 summarize the synthesis conditions of the macroinitiators and block copolymers. Our first attempts at acrylate−methacrylate block copolymers involved the extension of a poly(methyl methacrylate) (PMMA) macroinitiator with either BA or MA (Table

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Table 1. Conditions for PMMA Macroinitiator and Acrylate−MMA Block Copolymer Syntheses Using PMMA as Macroinitiator at 90 °C[a]

expt no.	amt of monomer (mL)	amt of solvent (mL)	[initiator] (M)	[CuX] (M)	[ligand] (M)	time (h)	M_n	M_w/M_n
1[b]	MMA (25)	DPE (25)	0.0468	0.0468 (0.01404)	0.01404	18.5	12 100	1.12
2[c]	BA (1.2)	DPE (1.2)	0.0346	0.0346	0.0692	21	19 000	1.15
3[d]	MMA (2.0)	DPE (2.0)	0.0467	0.0234	0.0467	16	11 000	1.10
4[e]	MA (0.9)		0.0556	0.0556	0.111	20	20 500	1.15
5[f]	MMA (0.6)	DPE (0.6)	0.0167	0.0083[g]	0.0167	20	37 600	1.90

[a] DPE = diphenyl ether. [b] Initiator = TsCl, CuX = $Cu^{II}Br_2$ and Cu^0 (in parentheses), L = dNbpy. [c] Initiator = PMMA (expt 1), CuX = CuCl, L = dNbpy. [d] Initiator = TsCl, CuX = CuBr, L = dNbpy. [e] Initiator = PMMA (expt 3), CuX = CuBr, L = dNbpy. [f] Initiator = PMMA-*b*-PMA-X (expt 4), CuX = CuBr, L = dNbpy. [g] Approximately 5 mg of Cu^0 added to reaction after 1.5 h.

Table 2. Conditions for PMA Macroinitiator and Acrylate−MMA Block Copolymer Synthesis Using PMA as Initiator[a]

expt no.	amt of monomer (mL)	amt of solvent (mL)	[initiator] (M)	[CuX] (M)	[ligand] (M)	temp (°C)	time (h)	M_n	M_w/M_n
6[b]	MA (10.0)		0.185	0.0925	0.0925	70	0.5	6 060	1.36
7[c]	MMA (5.0)	DPE (5.0)	0.0083	0.0166	0.0332	90	4.5	41 400	3.63
8[d]	MA (5.0)	EC (5.0)	0.111	0.0555	0.333	90	1.5	5 910	1.32
9[e]	MMA (5.0)	DPE (5.0)	0.0086	0.0172	0.0339	90	18	63 900	1.15
10[f]	BA (10.0)		0.01175	0.00816	0.0242	70	16	11 200	1.41
11[g]	MMA (1.0)	B (1.3)	0.0202	0.0409	0.0880	70	16	37 200	1.20

[a] DPE = diphenyl ether, EC = ethylene carbonate, B = benzene, MeXP = methyl 2-haloproprionate (halogen (X) = Cl or Br), PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine. [b] Initiator = MeClP, CuX = CuCl, L = PMDETA. [c] Initiator = PMA-Cl (expt 6), CuX = CuCl, L = dAbpy. [d] Initiator = MeBrP, CuX = CuBr, L = bpy. [e] Initiator = PMA (expt 8), CuX = CuCl, L = dNbpy. [f] Initiator = **1**, CuX = CuBr, L = dAbpy. [g] Initiator = PBA-Br (expt 10), CuX = CuCl, L = dAbpy.

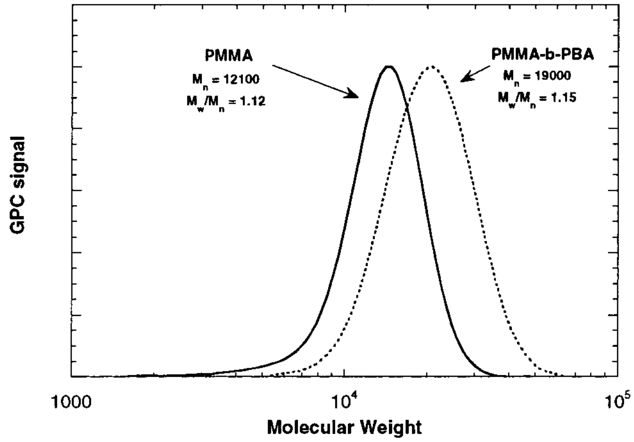


Figure 1. Molecular weight distributions of PMMA macroinitiator and PMMA-*b*-PBA diblock copolymer.

1). The first PMMA macroinitiator (expt 1) was synthesized according to the procedures given in previous reports,[11,16,17] using *p*-toluenesulfonyl chloride (TsCl) as an initiator and the CuBr/4,4′-di(5-nonyl)-2,2′-bipyridyl (dNbpy) catalyst system. The resulting polymer had M_n = 12 100 and M_w/M_n = 1.2. As we have shown before,[14] this synthesis leads to polymer containing a majority of Cl end groups (80−90%), with the balance being Br end groups. After purification, the PMMA sample was used as a macroinitiator for the ATRP of BA, again using CuBr/dNbpy as the catalyst (expt 2). The molecular weight distributions (MWDs) of the macroinitiator and resulting diblock copolymer are shown in Figure 1. The M_n of the copolymer was 19 000, with M_w/M_n = 1.15. The increase of the molecular weight, without a significant increase in M_w/M_n, indicates that effective initiation of ATRP of BA has taken place. Furthermore, there is no significant shoulder on the low molecular weight side of the MWD of the copolymer.

Another PMMA sample (expt 3), synthesized using TsCl/CuBr/dNbpy (M_n = 11 000 and M_w/M_n = 1.10), was used to initiate the ATRP of MA (expt 4). The MWDs of both the PMMA macroinitiator and PMMA-*b*-PMA block copolymer (M_n = 20 500 and M_w/M_n = 1.15) are shown in Figure 2. Again efficient initiation has taken place, and the polymerization appears to have proceeded in a controlled manner. This diblock copolymer was isolated and subjected to chain extension with MMA, in the hope of forming an ABA triblock copolymer (expt 5). The MWD of the ABA triblock is also shown in Figure 2 and clearly shows bimodality, with the higher molecular weight peak being quite broad. The final MWD gave M_n = 37 600 and M_w/M_n = 1.9. These observations are consistent with both slow and incomplete initiation of the second block of MMA by the PMMA-*b*-PMA macroinitiator. We have shown recently that some secondary halide compounds can be poor initiators of MMA because initiation may be slow relative to propagation.[12] In the present case, the end group of the diblock initiator is a secondary acrylate end (mostly) containing a Cl, which is less reactive than the tertiary MMA propagating center.

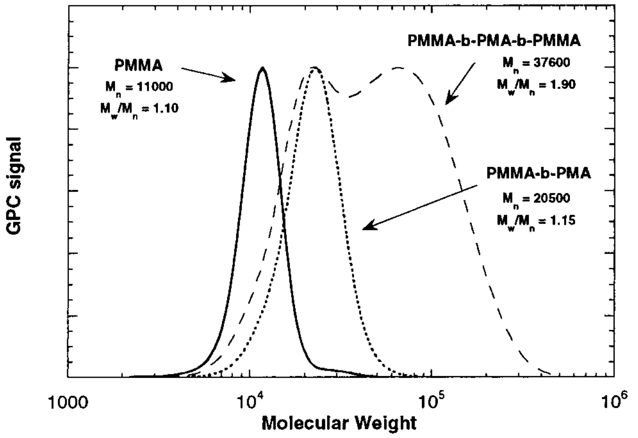


Figure 2. Molecular weight distributions of PMMA macroinitiator, PMMA-*b*-PMA diblock copolymer, and (attempted) PMMA-*b*-PMA-*b*-PMMA triblock copolymer.

The conclusion from these experiments is that PMMA is a good initiator for acrylates, but acrylates are not

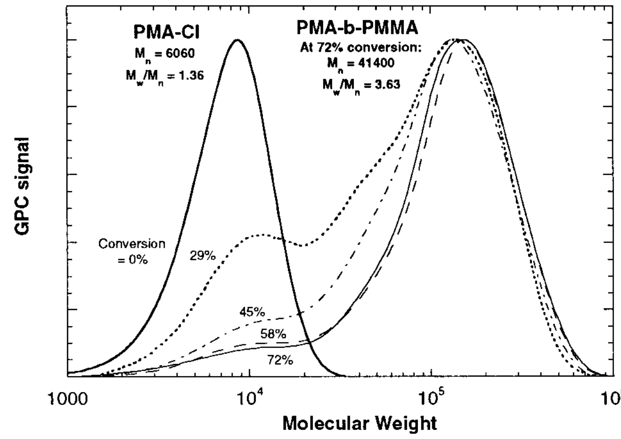


Figure 3. Molecular weight distributions of PMA-Cl macroinitiator and PMA-*b*-PMMA diblock copolymer at various monomer conversions (indicated in the figure).

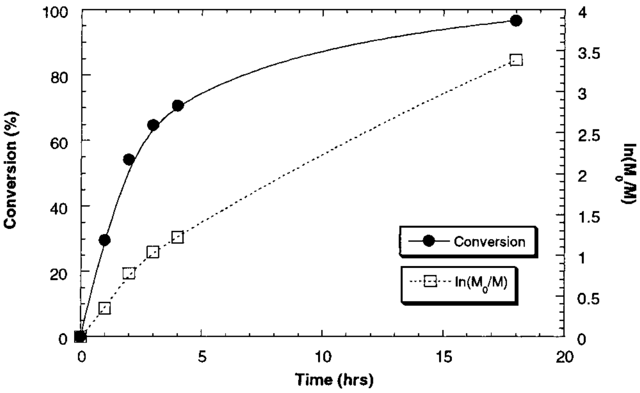


Figure 4. Conversion and semilogarithmic kinetic plot of the ATRP of MMA using PMA-Br as the intiator and CuCl/dNbpy as the catalyst (lines are to guide the eye only).

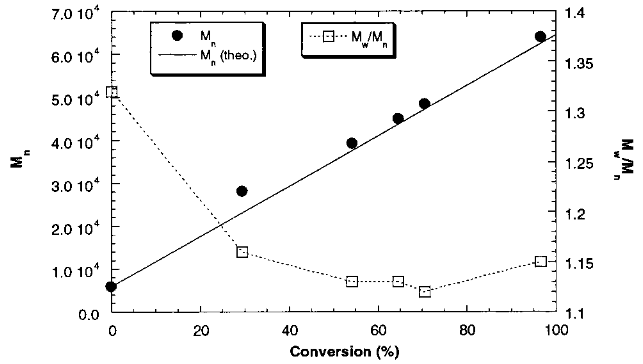


Figure 5. Molecular weight and polydispersity evolution as a function of conversion for of the ATRP of MMA using PMA-Br as the initiator and CuCl/dNbpy as the catalyst.

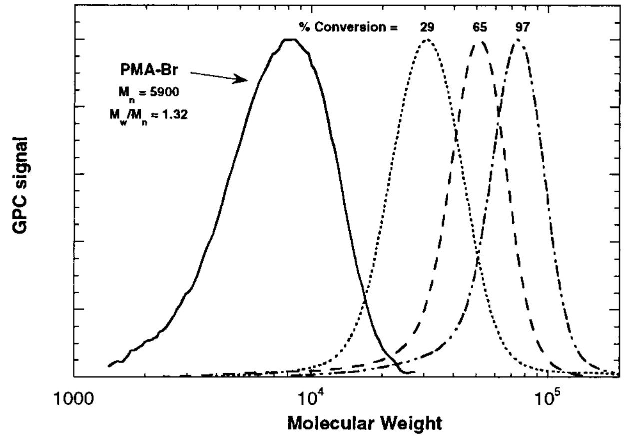


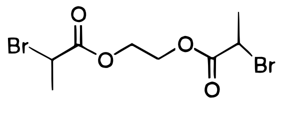
Figure 6. Molecular weight distributions of PMA-Br macroinitiator and PMA-*b*-PMMA diblock copolymer at various monomer conversions.

effective initiators for MMA polymerization when Cl is used as the halogen. We confirmed this by synthesizing a sample of PMA (expt 6, Table 2) that contained only Cl end groups (which was confirmed by ^{1}H NMR) and attempting to initiate MMA polymerization (expt 7). The MWDs of the macroinitiator and the product of the chain extension with MMA reaction as a function of monomer conversion are shown in Figure 3. Again, initiation is slow, as indicated by the broadness of the high molecular weight peak, the weak conversion dependence of the molecular weight of this peak, and the substantial amount of PMA macroinitiator remaining when over 70% of the monomer has been consumed.

To improve the initiation efficiency of the poly(acrylate) macroinitiators, we employed the technique of halogen exchange. We previously developed this technique to improve the initiation efficiency of benzyl halides (a secondary initiator) in the ATRP of MMA, where using benzyl bromide with CuCl increased the rate of initiation relative to the rate of propagation through halogen exchange.[14]

We therefore applied this method to the ATRP of MMA using a PMA macroinitiator that contained only Br end groups (expt 8). The PMA-Br was synthesized by using a Br-initiator and Cu^{I}Br catalyst, and the end-group functionality confirmed by ^{1}H NMR.[18] Samples were taken during the chain extension experiment (expt 9) at intervals to provide a picture of the kinetics of the reaction. Figure 4 shows how conversion and the semilog plot change with time. Conversion reached close to 100%, while the semilog plot is initially linear, and curved slightly at longer reaction times (this was observed in the ATRP of MMA before).[17] Figure 5 shows the linear increase in molecular weights and decrease in M_w/M_n as a function of conversion. The experimental molecular weights are in excellent agreement with the calculated theoretical molecular weights. The polydispersities decreased as the polymerization proceeded, indicating good control of the system, and remained below 1.15 beyond 50% monomer conversion. Figure 6 shows that there was complete initiation by the PMA macroinitiator and that the molecular weights progressively increased with time.

These results led us to synthesize PMMA containing Br end groups, to initiate acrylate ATRP and then subsequently use the diblock copolymer as an initiator for the ATRP of MMA, thus forming an ABA triblock copolymer. However, obtaining PMMA that had close to 100% functionality proved difficult, possibly because of side reactions that are more prevalent when Br is used as the end group than when Cl is the end group. One way of overcoming this was to synthesize the center block by first using a difunctional initiator, such as 1,2-bis(bromopropionyloxy)ethane[19] (**1**), and then add MMA



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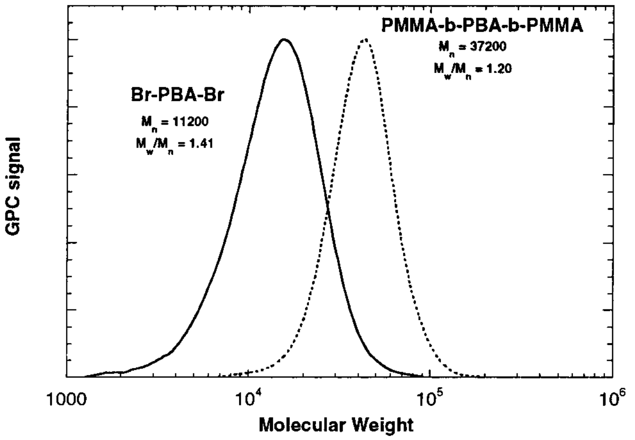

Figure 7. Molecular weight distributions of Br-PMA-Br macroinitiator and PMMA-*b*-PMA-*b*-PMMA triblock copolymer.

to both ends of the macroinitiator. This approach was used to synthesize difunctional poly(butyl acrylate) (PBA) (expt 10). This polymer was isolated and then added to MMA, CuCl, and dAbpy in benzene, and after 16 h produced a polymer with $M_n = 37\,200$ and $M_w/M_n = 1.2$ (expt 11). The MWDs of the difunctional PBA macroinitiator and the ABA triblock copolymer are shown in Figure 7. The chain extension is completely successful, with no sign of bimodality due to either poor initiation or only one end of the chain growing.

Conclusions

This paper has reported the successful synthesis of block copolymers, composed of acrylates and methacrylates, through ATRP. Using PMMA as the macroinitiator generally provides good initiation efficiency when the chain ends are nearly 100% functionalized. However, using polyacrylates as the macroinitiator requires that the end groups are Br and the catalyst is CuCl. This allows halogen exchange to occur, thus increasing the relative rate of initiation to propagation and giving a controlled polymerization. This was exemplified in the synthesis of a PMMA-*b*-PBA-*b*-PMMA triblock copolymer, where the difunctional center block was grown first and then MMA was added to both ends.

Experimental Section

Materials. Methyl methacrylate, butyl acrylate, and methyl acrylate were passed through an alumina column, dried over molecular sieves, deaerated by bubbling argon and stored under argon. Diphenyl ether was dried over molecular sieves and degassed with argon for 15 min before use. CuCl (98% Aldrich) and CuBr (98% Aldrich) were purified according to the literature procedure.[20] All the initiators were purchased from Aldrich and used as received. 4,4′-Di(5-nonyl)-2,2′-bipyridyl (dNbpy) and 4,4′-di(5-alkyl)-2,2′-bipyridyl (dAbpy; alkyl group is a mixture of C_5 and C_9 alkyl chains) were prepared by the procedure described in previous articles from this group.[5] Synthesis of 1,2-bis(bromopropionyloxy)ethane (**1**) has been reported elsewhere.[19] *N,N,N′,N′,N″*-Pentamethyldiethylenetriamine (PMDETA) was obtained from Aldrich and used without further purification.

General Procedures. Cu^IX (or $Cu^{II}Br_2$ and Cu^0) and ligand were placed in either a round-bottom or Schlenk flask, which was then purged with Ar. Monomer (and solvent if necessary) was introduced into the flask via an Ar-washed syringe. The flask was then placed in an oil bath at the appropriate temperature and the solution stirred until homogeneous. For the synthesis of macroinitiators, the alkyl halide (*p*-toluenesulfonyl chloride (TsCl) dissolved in monomer, methyl 2-chloropropionate (MeClP), or methyl 2-bromopropionate (MeBrP)) was then introduced into the flask via syringe. For block copolymer syntheses, the macroinitiator was either added to the flask in powder form with a positive Ar pressure or dissolved in a small amount of monomer or solvent and added to the reaction flask via syringe. The polymer was isolated by dissolving in tetrahydrofuran (THF) and passing through an alumina column and then isolated by either precipitation into methanol (PMMA-containing samples) or by evaporation of the monomer (and solvent where applicable).

Characterization. Polymer samples were dissolved in THF, passed through an alumina column, and filtered through a 0.2 μm PTFE filter. Molecular weights and molecular weight distributions were measured using a Waters 510 LC pump, Waters 712 WISP autosampler, Waters 410 differential refractometer and the following PSS GPC columns: 10^5 Å, 10^3 Å, and 100 Å. Molecular weights were calibrated using either poly(methyl methacrylate) (for PMMA homopolymers and block copolymers) or polystyrene (for poly(acrylate) homopolymers) standards. ^1H NMR spectra were measured in $CDCl_3$ on a Bruker AM 300 MHz spectrometer.

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