Bulk Synthesis of Poly(*tert*-butyl methacrylate) Long Macromonomer with Narrow Distribution by Atom Transfer Radical Polymerization and Nucleophilic Substitution

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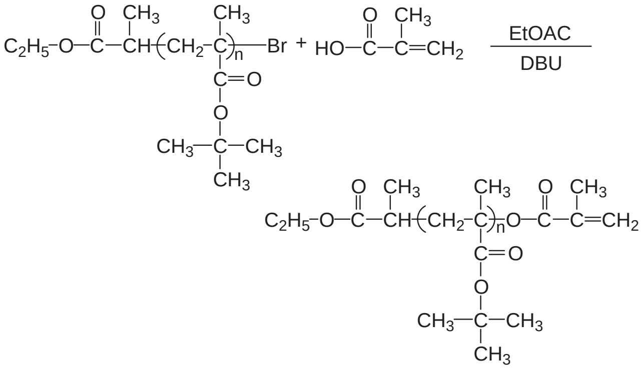
Poly(*tert*-butyl methacrylate) macrointermediates (PtBMA-Br) with a bromine atom end group were synthesized in the presence of the single ligand *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) by atom transfer radical polymerization (ATRP) in bulk. A macromonomer was successfully prepared by the nucleophilic substitution of the chain end to attain a high efficiency of C=C incorporation (89–92%; ^{1}H NMR). The macromonomer molecular weight was controlled to result in a high molecular weight (11000) with a narrow distribution of 1.20.

ATRP is a powerful tool to prepare polymers with predictable molecular weights and low polydispersities. Various polymers such as block copolymers,[1] graft copolymers,[2] and hyperbranched polymers[3] are available with this controllable radical polymerization. The functionalized polymers also can be obtained by ATRP by different approaches. There are main three ways to obtain the functionalized polymers; 1) polymerization of functionalized monomers,[4] 2) use of the functionalized initiator,[5] 3) chemical modification of the halogen end groups of the polymer.[6] The third method has the widest variety of the end group of these three methods because of no chemical hindrance of the incorporated functional group to the polymerization reaction. Especially, the bulk polymerization has the advantage of the reaction simplicity and purification expediency.

In this paper, we aim to prepare the long chain of poly(*tert*-butyl methacrylate) (PtBMA) macromonomer by the third method via the bulk ATRP. The long macromonomer can have a great advantage in the use of the small amount for preparation of functional polymeric nanosized particles[7–9] and graft copolymers. Although PtBMA has a high hydrolytic ability for conversion into amphiphilic or hydrophilic chains, there is no report on synthesis of the long PtBMA macromonomer with narrow distribution of molecular weight. Our procedure developed in this research could be briefly described in Scheme 1. Firstly, the PtBMA macrointermediate with a bromine atom end group (PtBMA-Br) was synthesized by ATRP. Then, the C=C group to the polymer chain end was incorporated by the nucleophilic substitution reaction of the terminal bromine with methacrylic acid (MAA).



Scheme 1. Syntheses of PtBMA macromonomer.

The typical procedure of the synthesis of PtBMA-Br through ATRP method was shown as follows: The ligand PMDETA (0.001 mol) and the tBMA monomer were added to a 100 mL three-neck round-bottom flask equipped with a magnetic bar and condenser which was pre-flushed with nitrogen. After the solution in the flask had been degassed with nitrogen for thirty minutes, the initiator ethyl 2-bromopropionate (EPN-Br) (0.5 mmol) was added via syringe, followed by addition of the catalyst CuCl (0.5 mmol). Then the flask was heated in an oil bath and stirred at 85 °C and degassed with nitrogen for additional 30 min, the flask was sealed with rubber septum and the reaction solution was stirred for a given period. The reaction proceeded homogeneously and the solution became somewhat viscous. The solution was cooled to room temperature spontaneously followed by THF addition (20 mL). CuCl was filtrated out by alumina filter, and then the yellow filtrate was poured slowly into the methanol/water (vol/vol = 1:1) to reprecipitate. The reprecipitation was repeated several times. The precipitates were dried in vacuo overnight, to yield the macrointermediate end-capped with a bromine atom.

The nucleophilic substitution of the terminal bromine in PtBMA-Br with methacrylic acid (MAA) to form PtBMA macromonomer with methacrylate end group was made as follows: PtBMA-Br was dissolved in ethyl acetate (EtOAc) (50%), and equimolar amount of MAA to the bromide was added under vigorous stirring and followed by the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The mixture was stirred for 24 h at 25 °C and then was reprecipitated over the mixed solvent of methanol/water (vol/vol = 1:1). The reprecipitation was repeated three times to wash out the unreactive MAA. The precipitates were dried in vacuo overnight, to produce the PtBMA macromonomer.

The number-average molecular weight, Mn, of PtBMA-Br could be controlled by changing the molar ratio of tBMA to initiator EPN-Br, the results are listed in Table 1. Mn increased linearly with the ratio of monomer to initiator to attain to a high value of 11000. These values were a bit smaller than calculated Mn presumably due to the restriction of chain propagation by the viscosity increased in the last stage. Besides, polydispersity index kept a low value within 1.20. The successful synthesis

Table 1. Molecular weight of PtBMA-Br macrointermediate[a]

Run	Molar Ratio[b]	Yield /%	$M_{n,cal}$ $/\times 10^{-4}$	$M_{n,GPC}$ $/\times 10^{-4}$	M_w/M_n
1	50:1	76	0.74	0.54	1.20
2	75:1	76	1.08	0.81	1.17
3	100:1	77	1.44	1.10	1.20

a) [PMDETA]:[CuCl]:[EPN-Br] = 2:1:1. b) [tBMA]:[EPN-Br].

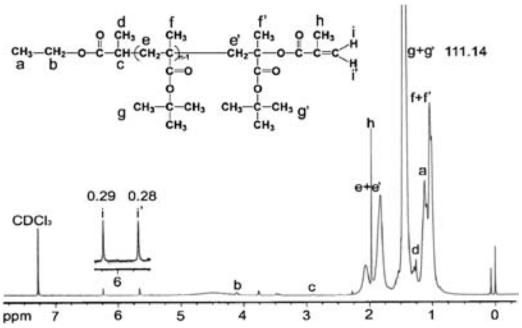


Figure 1. ^{1}H NMR spectra of PtBMA macromonomer.

of macrointermediates was made without bipyridine which was used with PMDETA in the literature.[6] This was quite meaningful in establishment of very simple bulk ATRP using only the single ligand of PMDETA.

Introducing C=C group to the PtBMA-Br end was the key step. Figure 1 shows the ^{1}H NMR spectra of macromonomer with the methacrylate end groups (recorded on a Bruker DMX500 in $CDCl_3$). The spectrum shows the methacrylate signals of CH_3– at a chemical shit, δ, of 1.9 ppm and of CH_2= at $\delta = 5.6$ and $\delta = 6.2$ ppm. On the other hand, the macrointermediate signal of $(CH_3)CBr$ at $\delta = 1.5$ ppm disappeared and the monomer tBMA signal of $=CH_2$ at $\delta = 5.5$ and $\delta = 6.0$ ppm was not detected. These results indicate that almost all of the C–Br bonds were successfully substituted into C=C group. Moreover, the introduction ratio of C=C group was calculated from the peak area of $=CH_2$ (peaks i and i′) with $-C(CH_3)_3$ (peaks $g + g'$) in Figure 1. The polymerization degree, $n = (M_n - M_{initiator})/M_{tBMA}$, could be evaluated by GPC (in Table 1). The integral ratio of peak area $S_{g+g'}/S_{i+i'}$ was calculated using GPC data by $(9H \times n)/2H$ under the assumption that complete substitution of bromines to MAA. The value was divided by the experimental value from NMR, to give the C=C introduction ratio. Repeated experiments show the introduction ratio ranged in 88.9–92.0%.

The polymerization ability of macromonomer was then affirmed by some experiments. The macromonomer PtBMA was homopolymerized (conditions: 1% AIBN, 60 °C, 24 h, in DMF) and M_n of the resulting poly(macromonomer)s were investigated by GPC (Figure S1 in Supporting Information). GPC curves show two peaks; the peaks at higher M_n position may be from the poly(macromonomer)s, and the peaks at lower M_n may be from unfunctionalized oligomers and unreacted macromonomers. GPC curves showed that an increase in the macromonomer M_n reduced the poly(macromonomer) M_n and increased the amount of unreacted macromonomers. Besides the copolymerization with MMA was successfully made. We can conclude that the macromonomers are successfully polymerized under certain conditions, although the polymerization efficiency of the increased macromonomer length was reduced.

The cross-linked poly(macromonomer) nanoparticles were prepared by dispersion terpolymerization of styrene (St, 0.01 mol), PtBMA macromonomer (0.015 mol % to St), and divinylbenezene (DVB, 0.9 mol % to total monomer) as a cross-linker (1 mol % AIBN, 5 mL ethanol, 60 °C). Dynamic light scattering (DLS) studies for the ethanol-dispersions of nanoparticles (10^{-5} g/L, 25 °C) showed that the nanoparticle size ranged in 90–350 nm with a narrow size distribution of ca. 1.20 and no aggregation was observed even after the more than 1 week still-standing (Figure S2 in Supporting Information). The size decreased with an increasing in macromonomer ratio and with an increase in the macromonomer length. This is the first example of cross-linker nanoparticles using long poly(macromonomer)s. Their properties are currently studying. Thus, we prepared the long macromonomer (M_n: 11000) with a narrow molecular weight distribution (1.2) by a simple bulk ATRP using a single ligand followed by the end substitution into MAA.

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