# Synthesis and Application of a Microgel-Supported Acylating Reagent by Coupled Ring-Opening Metathesis Polymerization and Activators Re-Generated by Electron Transfer for Atom Transfer Radical Polymerization

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A novel microgel-supported acylating reagent (MGAR) was prepared by combining ring-opening metathesis polymerization (ROMP) and Activators Re-Generated by Electron Transfer for Atom Transfer Radical Polymerization (ARGET ATRP): (1) synthesis of an ATRP macroinitiator **3** by living ROMP of oxanorbornene-based activated ester **1**, derived from *N*-hydroxysuccinimide, using the Grubbs initiator $RuCl_2(PCy_3)_2$(=CHPh) and (Z)-but-2-ene-1,4-diyl bis(2-bromopropanoate) (BDBP) as a terminating agent; (2) synthesis of MGAR **4** by ARGET ATRP of styrene (S) and divinylbenzene (DVB) using the prepared macroinitiator **3**, a $CuCl_2$/$Me_6$TREN (tris[2-(dimethylamino)ethyl]amine) catalyst system, a $Sn(Oct)_2$ [tin(II)2-ethylhexanoate] reducing agent. The synthesized microgels **4** exhibit excellent acyl (acetyl, benzoyl, phenylsulfonyl) transfer properties for primary and secondary amines (*n*-$BuNH_2$, $Et_2NH$, morpholine, etc.) under mild conditions (25 °C, 13.5−14 h) affording *N*-acylamines with high yield (95.6−100%) and purity (94.1−96.0%).

## Introduction

In recent years the interest in polymer-supported reagents for organic synthesis has significantly increased along with the rapid development of the combinatorial chemistry.[1,2] Typically, the insoluble polymers are the most commonly used because of the well-known advantages such as the ease of isolating the used polymer from a reaction mixture, the adaptation of the supported reagents for continuous-flow process, and so forth. However, the heterogeneous nature of the reaction in the use of these solid phase polymers in solution brings about some drawbacks, such as the difficulty of monitoring the reaction process, the low accessibility of the anchored reagents to the substrates in solution, in general the non-linear reaction kinetics and so forth. Consequently, soluble polymer supported reagents have recently attracted considerable attention.[3−8] The soluble polymer reagents behave like small molecules in solution affording the normal solution reaction kinetics, convenience in monitoring the reaction process, higher reaction efficiency, and so forth.

Acylation of amines is one of the most commonly used reactions in the pharmaceutical and fine chemical synthesis.[9−17] Ring-opening metathesis polymerization (ROMP) proved to be a useful tool for functional polymer design;[18−24] among the diversity of functional polymers synthesized by means of ROMP over the past decade, the ROMPGEL-supported acylating reagents reported by Barrett et al. represent a promising category of insoluble functional polymers.[25−28] It is also worth noting that in the field of soluble functional polymers, the pioneering work on microgel-supported organic synthesis reported by Wulff and Janda is encouraging.[29−31] Microgels are intramolecularly cross-linked molecules in nature; interestingly they form stable solutions of low viscosity in suitable solvents. At this point, microgels are the clever hybrids of insoluble and soluble polymers. The unique properties of microgels make them seem to be more suitable candidates as soluble supports for organic synthesis. Herein, we report the first synthesis of a microgel-supported acylating reagent (MGAR) by coupled ROMP and ARGET ATRP (controlled polymerization using **A**ctivators **R**e-**G**enerated by **E**lectron **T**ransfer for **A**tom **T**ransfer **R**adical **P**olymerization),[32−34] and the application of the microgel reagent to acylation of amines.

## Results and Discussion

**Synthesis of MGAR.** The synthesis of MGAR **4** contains two key polymerization processes (Scheme 1).

First, the ROMP of monomer **1**, derived from an activated ester, oxanorborneno-succinimidyl carboxylate, was carried out at room temperature (RT) in dichloromethane (DCM) using a Grubbs initiator $RuCl_2(PCy_3)_2$(=CHPh). Termination of the active ruthenium carbene end of the ROM-polymer **2** with cis-2-butene-1, 4-diyl bis(2-bromopropanoate) (BDBP) yielded a monoend α-bromoester-functionalized polymer **3** with designed number-average molecular weight($M_n$). The ROMP showed typical characteristics of living polymerization: the formed polymers possessed narrow molecule weight distribution (MWD) as evidenced by the polydispersity index

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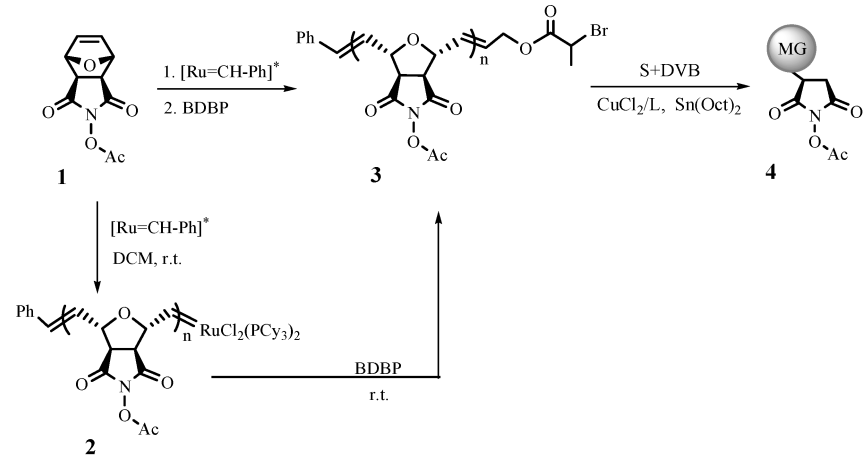
**Scheme 1.** Synthesis of MGAR[a]




Ac: PhCO (**a**), $CH_3CO$ (**b**), $PhSO_2$ (**c**); [Ru=CH-Ph]*: $RuCl_2(PCy_3)_2$(=CH-Ph); L: $Me_6TREN$.

**Table 1.** Synthesis of an ATRP Initiator of Polymer **3a** by ROMP[a]

| entry | $[M]_0/[I]_0$[b], mole/mole | conv.[c], % | $M_{n,th} \times 10^{-3}$ | $M_{n,GPC} \times 10^{-3}$ | PDI |
|---|---|---|---|---|---|
| 1 | 10 | 99.9 | 3.12 | 3.60 | 1.08 |
| 2 | 20 | 99.6 | 5.97 | 5.70 | 1.11 |
| 3 | 25 | 99.6 | 7.40 | 7.70 | 1.13 |
| 4 | 50 | 99.8 | 14.5 | 13.0 | 1.14 |
| 5 | 100 | 99.7 | 28.8 | 27.4 | 1.19 |

[a] Polymerization in DCM, at RT for 20 min. [b] M: monomer **1a**; I: $RuCl_2(PCy_3)_2$(=CH-Ph). [c] Measured by $^1H$ NMR.

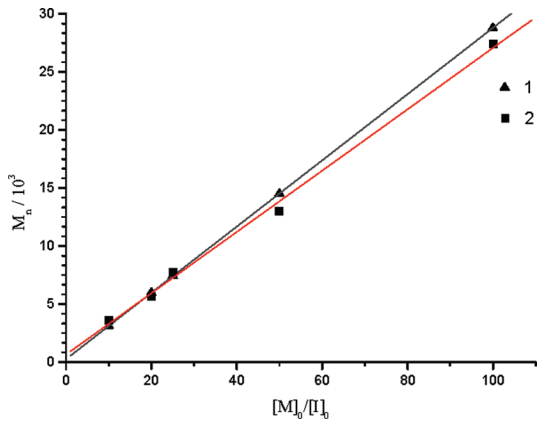



**Figure 1.** Synthesis of an ATRP Macroinitiator **3a** by ROMP.

(PDI 1.08−1.19, Table 1) values, a linear relationship of $M_{n,GPC}$ ($M_n$ measured by GPC) of formed polymers versus the initial molar ratio of $[M]_0/[I]_0$ was observed (Figure 1, line 2), and the determined values of $M_{n,GPC}$ were approaching the theoretically calculated values of $M_{n,th}$ (Figure 1, line 2 vs 1).

Second, to prepare the MGARs the preformed polymers **3** (**3a-3**: $M_n$ 7.70 $\times$ $10^3$; **3b**: $M_n$ 1.10 $\times$ $10^4$; **3c**: $M_n$ 8.45 $\times$ $10^3$, in Table 1 Entry 3, Supporting Information Table SI-1 Entry 4, Table SI-2 Entry 3, respectively) were used to initiate an ARGET ATRP of styrene and divinylbenzene in DMF using a $CuCl_2$/$Me_6TREN$ catalyst system and a reducing agent tin(II) 2-ethylhexanoate $Sn(Oct)_2$. Under the selected optimizing conditions ($[DVB]_0/[S]_0$ = 0.20, 100 °C, 24 h) the target MGARs **4a-2** ($M_n$ 4.21 $\times$ $10^5$), **4b** ($M_n$ 6.16 $\times$ $10^5$), and **4c** ($M_n$ 4.35 $\times$ $10^5$) were successfully prepared

**Table 2.** Synthesis of MGARs by ARGET ATRP with Synthesized Macroinitiators[a]

| entry | I | $[DVB]_0/[S]_0$ mol/mol | *t*, h | MGAR | $M_{n,GPC} \times 10^{-5}$ | PDI | $Cd_e$[b] % | solubility DMF |
|---|---|---|---|---|---|---|---|---|
| 1 | 3a-3 | 0.20 | 22.0 | 4a-1 | 3.84 | 1.81 | 4.5 | sol. |
| 2 | 3a-3 | 0.20 | 24.0 | 4a-2 | 4.21 | 1.78 | 4.8 | sol. |
| 3 | 3a-3 | 0.30 | 24.0 | 4a-3 | | | | insol. |
| 4 | 3a-3 | 0.40 | 23.8 | 4a-4 | | | | insol. |
| 5 | 3b-4 | 0.20 | 24.0 | 4b | 6.16 | 1.98 | 4.6 | sol. |
| 6 | 3c-3 | 0.20 | 24.0 | 4c | 4.35 | 1.74 | 4.4 | sol. |

[a] 100 °C, DMF 2 mL, $[I]_0$ = 3.167 mmol/L; I: macroinitiator; $[S]:[I]:[CuCl_2]:[Me_6TREN]:[Sn(Oct)_2]$ = 500:1:0.01:0.1:0.1. [b] Cross-linking degree quantitatively estimated by $^1H$ NMR.

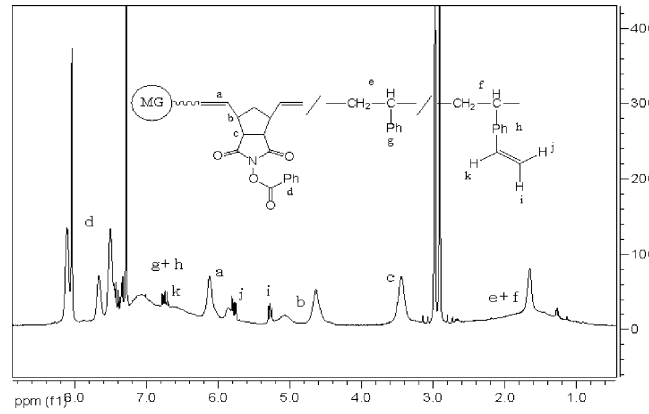


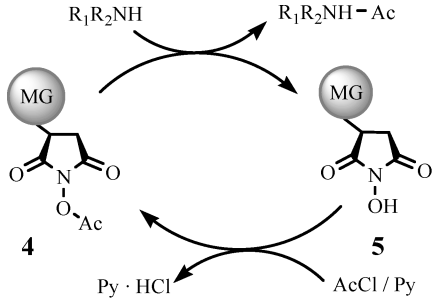

**Figure 2.** $^1H$ NMR Spectrum of MGAR **4a-2**

(Table 2, Entry 2, 5, 6). $^1H$ NMR characterization demonstrated the structure of synthesized MGARs as exemplified by MGAR **4a-2** (Figure 2).

Experimental results indicated that the optimizing value of $[DVB]_0/[S]_0$ was 0.20. A further increase of initial DVB feeding led to the formation of insoluble polymers instead of soluble microgels (Table 2, Entry 3, 4). The cross-linking degrees of the microgel reagents were quantitatively estimated to be 4.4−4.8% (Table 2) based on the $^1H$ NMR characterization of the amount of unreacted C=C bonds in the DVB units of the microgel molecules.

**Application and Recycle of MGAR.** The synthesized microgels **4** were applied to N-acylation of a variety of amines (Scheme 2, Table 3).

**Scheme 2.** Application and Recycle of Synthesized MGARs




Ac: PhCO, $CH_3CO$, $PhSO_2$
$R_1R_2NH$: n-$BuNH_2$, $Et_2NH$, Morpholine, $NH_2$-Et-$NH_2$, et al.

**Table 3.** Acylation of Amines Using Synthesized MGARs[a]

| | MGAR | | amine | | | | |
|---|---|---|---|---|---|---|---|
| entry | no. | μmol | name | μmol | time, h | yield % | purity[b] % |
| 1 | 4a-2 | 198 | *n*-$BuNH_2$ | 152.3 | 13.5 | 100 | 96.0 |
| 2 | 4a-2 | 132 | $Et_2NH$ | 96.25 | 14.0 | 96.1 | 94.1 |
| 3 | 4a-2 | 132 | Morpholine | 103.3 | 14.0 | 96.7 | 95.1 |
| 4 | 4a-2 | 133 | $NH_2$-Et-$NH_2$ | 104.6 | 14.0 | 93.7[c] | |
| 5 | 4a-2 | 133 | *p*-phenetidine | 100.9 | 18.0 | 0 | |
| 6 | 4a-2 | 133 | Pyrrole | 101.2 | 18.0 | 0 | |
| 7 | 4b | 132 | *n*-$BuNH_2$ | 101.3 | 13.5 | 98.1 | 94.7 |
| 8 | 4b | 133 | $Et_2NH$ | 96.25 | 13.5 | 96.5 | 95.3 |
| 9 | 4b | 133 | Morpholine | 103.3 | 13.8 | 97.2 | 95.4 |
| 10 | 4b | 132 | $NH_2$-Et-$NH_2$ | 104.6 | 14.0 | 93.4[d] | |
| 11 | 4c | 132 | *n*-$BuNH_2$ | 101.3 | 13.5 | 97.6 | 94.5 |
| 12 | 4c | 132 | $Et_2NH$ | 96.25 | 13.5 | 95.6 | 95.2 |
| 13 | 4c | 133 | Morpholine | 103.3 | 14.0 | 96.2 | 94.3 |
| 14 | 4c | 133 | $NH_2$-Et-$NH_2$ | 104.6 | 14.0 | 94.0[e] | |

[a] Temp. 25 °C, THF. [b] Based on $^1$H NMR characterization. [c] Product contained monoacylated product 84.0% and bis-acylated product 9.7%. [d] Product contained monoacylated product 83.5% and bis-acylated product 9.9%. [e] Product contained monoacylated product 84.5% and bis-acylated product 9.5%.

Acylation of primary and secondary amines (*n*-$BuNH_2$, $Et_2NH$, morpholine, etc.) with the synthesized MGARs was successfully carried out under mild conditions (25 °C, 13.5−14 h) in THF with a slight excess equivalency of microgel agents yielding the desired products in high purity (94.1−96.0%) and excellent yield (95.6−100%, Table 3). However, the acylation products of diamine $H_2NCH_2CH_2NH_2$ contained a small amount of 1,2-bis-acylated compounds (10.1−10.6% of the total yields). It is also worth noting that an attempt at acylating *p*-phenetidine and pyrrole with MGAR **4a-2** failed (Table 3, Entry 5, 6). This is possibly because the acylation reaction of amines is a nucleophilic substitution. A key step in the reaction is the attack of N atoms of the nucleophilic substrates (amines) upon the carbonyl carbons in MGAR molecules. The nucleophilicities of nitrogen atoms in *p*-phenetidine and pyrrole are greatly decreased owing to the p-$\pi$ conjugation of p-lone pair electrons of N atoms with the $\pi$-electrons in the benzene and pyrrole rings.

The traditionally insoluble reactive polymers prepared by copolymerization of a functional monomer and a cross-linking agent are macroreticular beads or granules. In the use of these polymers, a considerable portion of anchored functional groups are difficult to access by substrates in solution. The MGAR **4**, reported herein, was prepared by the controlled radical polymerization (ARGET ATRP) using a macroinitiator **3**, a linear functional polymer prepared by living ROMP; the molecular geometry of the MGAR **4** is postulated to bear a resemblance with that of star polymers (Scheme 3). The functional groups are anchored on the naked arms of the microgels and hence are readily accessed by substrates in solution. This may account for the excellent acyl transfer performance of the MGAR.

Because of the high molar mass of the synthesized MGARs (**4a-2**: $M_n$ 4.21 × $10^5$; **4b**: $M_n$ 6.16 × $10^5$; **4c**: $M_n$ 4.35 × $10^5$), the used microgels **5** can be conveniently recovered by precipitation from methanol. Treating the recovered microgels **5** with corresponding acyl chlorides regenerates the microgel reagents **4**. On the basis of $^1$H NMR characterization, the relative functionalization degrees of the regenerated microgel reagents (Table 4, **R-4a-2**, **R-4b**, **R-4c**) were quantitatively estimated to be 70.4−72.5%. The acylation performance of the regenerated MGARs for amines showed no obvious difference with that of the freshly prepared counterparts (Table 4).

## Conclusion

In summary, a new method for making microgel-supported reagents was demonstrated. The approach involves the following. (1) Synthesis of an ATRP macroinitiator **3**, a linear polymer bearing a side activated acyl group in the repeating unit and a chain-end α-bromoester group, via living ROMP with Grubbs initiator $RuCl_2(PCy_3)_2$(=CH-Ph). (2) To prepare the microgel reagent **4**, ARGET ATRP of styrene and divinylbenzene using the synthesized macroinitiator was carried out in DMF. Three kinds of acyl (acetyl, benzoyl, phenylsulfonyl) transfer reagents supported on microgels with high molar mass (**4a-2**: $M_n$ 4.21 × $10^5$; **4b**: $M_n$ 6.16 × $10^5$; **4c**: $M_n$ 4.35 × $10^5$) and narrower MWD (**4a-2**: PDI 1.78; **4b**: PDI 1.98; **4c**: PDI 1.74) were successfully prepared. Under mild conditions the microgel reagents showed excellent acylating properties for primary and secondary amines affording the desired products with very high yield and purity. For ethylene diamine the acylated products contaminated with 10.1−10.6% of bis-acylated compounds. An attempt at acylating *p*-phenetidine and pyrrole (weak base amines possessing p-$\pi$ conjugation) with MGAR **4a-2** failed. Finally, it is worth noting that the microgels can be easily recovered after use, and the regenerated microgel reagents showed similar acylation performance as the freshly prepared counterparts. The results of the work presented here reveal the promising prospect of microgel-supported reagents in organic synthesis. To the best of our knowledge, this is the first report on the synthesis and application of a microgel-supported acylating reagent.

## Experimental Section

**Materials and General Methods.** All manipulations and reactions were carried out under argon with standard Schlenk apparatus and techniques. Grubbs complex $RuCl_2(PCy_3)_2$-(=CH-Ph), *N*-hydroxysuccinimide(97%) and tin(II) 2-ethylhexanoate were products of Sigma-Aldrich Co., BDBP was prepared according to ref 35, and $Me_6$TREN was synthesized according to a literature procedure.[36] Other reagents were analytically pure and thoroughly dried before use. Dry,

**Scheme 3.** Plausible Pathway on the Synthesis of MGAR by Coupled ROMP and ARGET ATRP

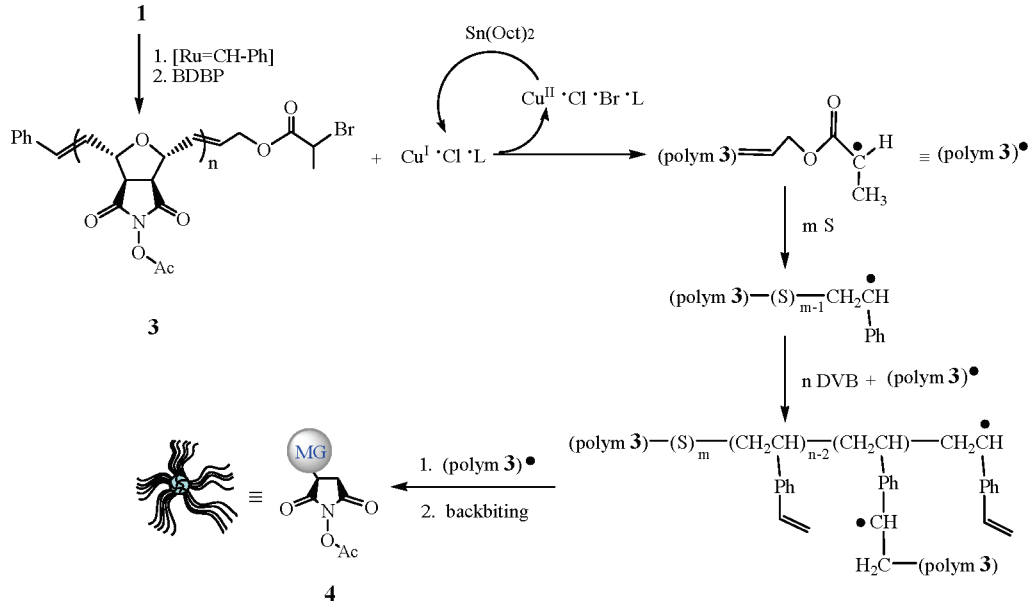



**Table 4.** Reusability of the Regenerated MGARs[a]

| | | | *N*-acylbutylamine | | *N*-acyldiethylamine | |
|---|---|---|---|---|---|---|
| entry | microgel | func. degree[e] mole % | yield (%) | purity (%) | yield (%) | purity (%) |
| 1 | 4a-2 | 100 | 100 | 96.0 | 96.1 | 94.1 |
| 2 | R-4a-2[b] | 70.4 | 97.0 | 94.1 | 94.5 | 93.2 |
| 3 | 4b | 100 | 98.1 | 94.7 | 96.5 | 95.3 |
| 4 | R-4b[c] | 71.2 | 96.3 | 93.8 | | |
| 5 | 4c | 100 | 97.6 | 94.5 | 95.6 | 95.2 |
| 6 | R-4c[d] | 72.5 | 95.8 | 94.2 | 93.8 | 93.6 |

[a] 25 °C, 13.5 h, THF. [b] **R-4a-2**: regenerated MGAR **4a-2**. [c] **R-4b**: regenerated MGAR **4b**. [d] **R-4c**: regenerated MGAR **4c**. [e] Relative value.

oxygen-free solvents were used throughout the experiments. The molecular weights of the synthesized polymers were determined with GPC on a Water 1525 chromatograph equipped with a refractive-index detector and a set of three columns (styragel HT2, HT3, HT4). The columns were calibrated with polystyrene standards. Analysis was performed with THF as a solvent at a flow rate of 1.0 mL/min. $^1$H NMR spectra of the samples were recorded on a Varian Unity Plus-400 spectrometer operating at 400 HMz ($^1$H).

**Preparation of Monomer 1.** The typical procedure is as follows**:** An oven-dried flask was charged with *N*-hydroxysuccinimide (2.03 g, 11.22 mmol) in 10 mL of DMF. Benzoyl chloride (1.6 mL, 13.90 mmol) was added dropwise into the flask. The mixture was stirred at 60 °C for 7 h, then poured into 100 mL of water. The white solid was filtered out, washed with water for three times, then vacuum-dried at 40 °C for 24 h. A white solid (3.08 g) was obtained in 96.3% yield. $^1$H NMR($CDCl_3$, 400 MHz) $\delta$: 2.966(s, 2H), 5.394(s, 2H), 6.559(s, 2H), 7.492−7.530(t, $J$ = 7.6 Hz, 2H), 7.660−7.697(t, $J$ = 7.6 Hz, 1H), 8.122−8.141(d, $J$ = 7.6 Hz, 2H).

**Preparation of Macroinitiator 3.** The general procedure is as follows: Grubbs Catalyst ($RuCl_2(PCy_3)_2$(=CH-Ph)) (0.2094 g, 0.2544 mmol, 4 mol %) in 4 mL of $CH_2Cl_2$ was added to a stirred solution of **1a** (1.8145 g, 6.3758 mmol) in 7.5 mL of $CH_2Cl_2$. The mixture was stirred at 25 °C for 20 min. BDBP (0.7351 g, 2.0534 mmol) in 2 mL of $CH_2Cl_2$ was added to the mixture at RT, and stirring was kept up for another 20 min. The polymer-containing solution was added dropwise to a mixed solution of ethyl ether and *n*-hexane (1:1, 100 mL). Filtration followed by vacuum-drying yielded a pale brown powder 1.6252 g in 89.6% yield. GPC: $M_n$ = 7.7 × 10$^3$, $M_w/M_n$ = 1.13. $^1$H NMR($CDCl_3$, 400 MHz) $\delta$: 3.416(br, s, 2nH), 4.373−4.438(m, 1H), 4.620−5.065(2br, 2s, (2n+2)H), 5.834−6.102(2br, 2s, 2nH), 6.299−6.353(m, 2H), 6.766−6.819(m, 1H), 7.487(br, s, 2nH), 7.650(br, s, 1nH), 8.099(br, s, 2nH).

**Preparation of MGAR 4.** The typical procedure is as follows: Macroinitiator **3a-3** (Mn = 7700, PDI = 1.13, 0.2432 g, 31.67 $\mu$mol), styrene(S, 1.71 mL, 14.80 mmol) and divinylbenzene (DVB, 550 $\mu$L, 80%, containing S 0.952 mmol and DVB 3.131 mmol) were added to DMF (10 mL). A DMF solution of $CuCl_2$ and $Me_6$TREN (265 $\mu$L, [$CuCl_2$] = 1.1852 mmol/L, [$Me_6$TREN]/[$CuCl_2$] = 10:1), and a toluene solution of Sn(Oct)$_2$ (50 $\mu$L, [Sn(Oct)$_2$] = 30.916 mmol/L) were added to the above mixture. After stirring for 24 h at 100 °C under argon, the reaction mixture was poured into methanol (200 mL). A pale yellow powdery polymer was precipitated and was filtered, washed with methanol, and vacuum-dried yielding the desired microgel **4a-2** 0.8017 g. GPC: $M_n$ = 4.21 × 10$^5$, $M_w/M_n$ = 1.78. $^1$H NMR($CDCl_3$, 400 MHz) $\delta$: 0.4−2.6(br, 3.76H), 3.446(br, s, 2H), 4.640−5.080(2br, 2s, 2H), 5.255−5.299(dd, $J_1$ = 10.4 Hz, $J_2$ = 7.2 Hz, 0.25H), 5.753−5.813(dd, $J_1$ = 17.6 Hz, $J_2$ = 6.4 Hz, 0.29H), 5.858−6.121(2br, 2s, 2H), 6.257−7.255(br, 3.81H), 6.711−6.782(dd, $J_1$ = 17.6 Hz, $J_2$ = 10.8 Hz, ∼0.25H), 7.506(br, s, 2H), 7.667(br, s, 1H), 8.113(br, s, 2H).

**Acylation of Amines.** The general procedure is as follows: To a solution of MGAR **4a-2** (0.1860 g, containing benzoyl group 198.0 $\mu$mol) in 2 mL of THF *n*-butylamine (15 $\mu$L, 152.3 $\mu$mol) was added. Then the reaction mixture was stirred at 25 °C for 13.5 h. Four milliliters of methanol was added to the mixture, and the precipitated polymer was filtered off, vacuum-dried to afford a pale yellow powder (0.1575 g, 92.5% polymer recovery). The filtrate was

evaporated under vacuum to remove the solvent affording *N*-benzoylbutylamine (27.2 mg) in 100% yield and 96.0% purity. $^1$H NMR($CDCl_3$, 400 MHz) $\delta$: 0.955−0.992(t, $J$ = 7.2 Hz, 3H), 1.386−1.479(m, $J$ = 7.2 Hz, 2H), 1.579−1.654(m, $J$ = 7.2 Hz, 2H), 3.450−3.500(q, $J$ = 7.2 Hz, 2H), 6.084(s, 1H), 7.418−7.454(t, $J$ = 7.2 Hz, 2H), 7.481−7.518(t, $J$ = 7.2 Hz, 1H), 7.753−7.771(d, $J$ = 7.2 Hz, 2H).

**Regeneration of MGAR 4.** The general procedure is as follows: To a solution of recovered microgel **5** (70.60 mg) in pyridine (2 mL) benzoyl chloride (45 $\mu$L, 0.390 mmol) was added. The mixture was stirred at RT for 24 h, then 4 mL of methanol was added into the mixture. The precipitated polymer was filtered off, washed with cold methanol, and vacuum-dried affording microgel **R-4a-2** 0.0641 g (yield: 81.75%), with a relative functionalization degree of 70% based on $^1$H NMR characterization. $^1$H NMR($CDCl_3$, 400 MHz) $\delta$: 0.4−2.6(br, ∼3.41H), 3.425(br, s, 2H), 4.624−5.062(2br, 2s, 2H), 5.830−6.104(2br, 2s, 2H), 6.250−7.230(br, 3.45H), 7.477(br, s, 1.40H), 7.642(br, s, 0.69H), 8.084(br, s, 1.39H).

**Reusability of Regenerated MGAR.** The general procedure is as follows: To a solution of regenerated microgel **R-4a-2** (0.0476 g, 36.65 $\mu$mol) in THF (2 mL) was added *n*-butylamine (2.7 $\mu$L, 28.20 $\mu$mol). The mixture was stirred at 25 °C for 13.5 h, then 4 mL of methanol was added. The precipitated polymer was filtered off and vacuum-dried to afford a pale yellow fine powder (0.0403 g, 90.06% polymer recovery). The filtrate was evaporated under vacuum to remove the solvent affording *N*-benzoylbutylamine (0.0047 g, yield: 97.0%, purity: 94.1%). $^1$H NMR($CDCl_3$, 400 MHz) $\delta$: 0.946−0.983(t, $J$ = 7.2 Hz, 3H), 1.377−1.469(m, $J$ = 7.2 Hz, 2H), 1.572−1.646(m, $J$ = 7.2 Hz, 2H), 3.441−3.491(q, $J$ = 7.2 Hz, 2H), 6.114(s, 1H), 7.411−7.448(t, $J$ = 7.2 Hz, 2H), 7.476−7.512(t, $J$ = 7.2 Hz, 1H), 7.748−7.766(d, $J$ = 7.2 Hz, 2H).

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**Supporting Information Available.** Experimental data on synthesis of ATRP macroinitiators of polymer **3b** and **3c** by ROMP; $^1$H NMR spectra of monomers **1a**, **1b**, and **1c**, macroinitiator **3a-3**, BDBP, *N*-benzoylbutylamine, *N*-benzoyldiethylamine, *N*-acetylmorpholine, and *N*-phenylsulfonylmorpholine; GPC traces of macroinitiators **3a-3**, **3b-4**, **3c-3**, and microgel **4a-2**; $^1$H NMR Spectra of MGAR **4a-2** and Regenerated MGAR **R-4a-2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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