Macromolecules

Article

pubs.acs.org/Macromolecules

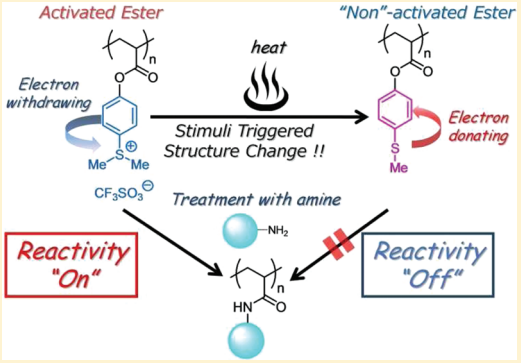
Changing the Reactivity of Polymeric Activated Esters by Temperature: On−Off Switching of the Reactivity of Poly(4-acryloxyphenyldimethylsulfonium triflate)

Ryohei Kakuchi and Patrick Theato*

Institute for Technical and Macromolecular Chemistry, University of Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany

Supporting Information

ABSTRACT: RAFT polymerization of 4-acryloxyphenyldimethylsulfonium triflate (SR-AEM) using pentafluorophenyl-(4-phenylthiocarbonylthio-4-cyanovalerate) as the chain transfer agent and AIBN as a radical source in acetonitrile at 90 °C yielded poly(4-acryloxyphenyldimethylsulfonium triflate) (poly(SR-AEM))s in high yields with well-controlled molecular weights and polydispersity indices. The reactive polymer poly(SR-AEM) was converted using an excess amount of amines, e.g., isopropylamine yielding predominantly poly(*N*-isopropylacrylamide) with defects of poly(4-acryloxyphenyl methylsulfide) in a minor ration of less than 16%. Furthermore, poly(SR-AEM) could be converted by thermo-triggered release of methyl group at dimethylsulfonium ion group to afford poly(4-acryloxyphenyl methylsulfide) (poly(APM)) as proved by ^{1}H NMR measurements, which did not react with amines anymore. To the best of our knowledge, this represents the first temperature-induced "on−off switching" of the reactivity of an activated ester by using 4-dimethylsulfonim phenol as the stimuli-responsive leaving group.



INTRODUCTION

In a growing area of functional polymer science, polymers with readily clickable groups receive increasing attention because of their robust and reliable ability to yield functional materials such as bio-related polymers. Such post-polymerization processes can be conducted not only in solution but also on surfaces.[1−19] To expand the scope of click ready functional materials, many click type reactions have been utilized. This includes Cu(I)-catalyzed[12] and metal-free[2] 1,3-dipolar cycloaddition reactions between organo-azides and acetylenes as well as thiol−ene,[8] thiol−maleimide,[9] isocyanate−nucleophile,[17−19] and activated ester−amine[16] reactions, which all practically lead to quantitative conversions during the post-polymerization modification step. Although the variety in reactants, catalyst, and reaction conditions can be varied, the click reaction site itself provides only a fixed reactivity toward certain molecules. Hence, incorporation of different functionalities into a polymer by post-polymerization modifications has been achieved by orthogonal click reaction sites, which eventually leads to orthogonally functionalized block copolymers.[20−24]

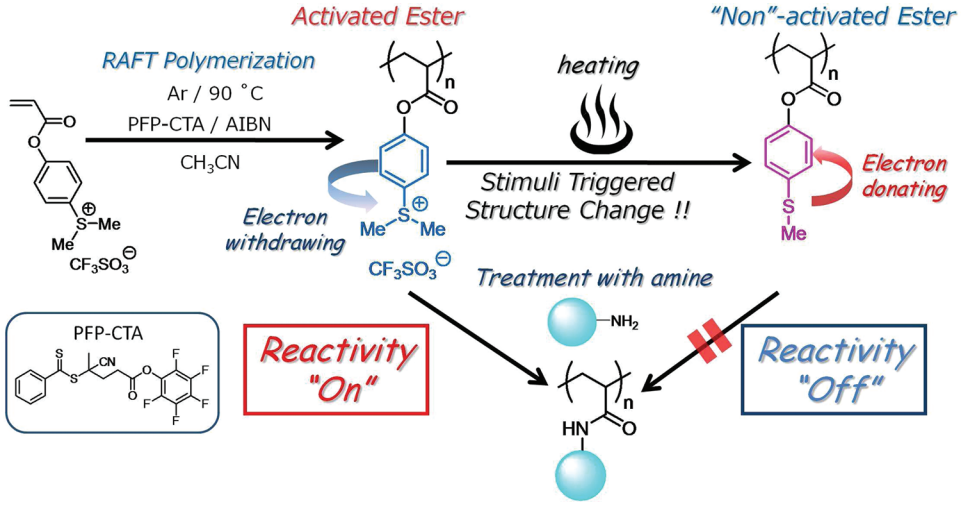
Among the number of functionalities that are potentially useful in material science, polymers with stimuli responsive properties are particular appealing.[25] When such stimuli responsive properties could be combined with a click reactivity, stimuli-induced switching of reactivity in click chemistry is rationally expected, which would lead to a new functionalization methodology for polymer scientists. Despite the great importance and potential of stimuli triggered reactivity switching for click type reactions, almost no attention has been paid to this synthetic area yet. While poly(4-vinylbenzoyl azide) could be used to generate isocyanate groups upon heating,[26] i.e., showing in principle the possibility of temperature-responsive functionalization, it was Locklin and co-workers who reported a photoresponsive polymer film consisting of cyclopropenone as a photoresponsive clickable reaction site, and they succeeded in a spatially controlled functionalization.[27] However, cyclopropenone-based click chemistry suffers from the difficulty of the monomer synthesis.[28] Furthermore, it was unfortunate that neither conversions were reported nor any reaction in solution investigated.[27]

In order to realize an external-stimuli triggered reactivity switching for click type reactions, phenoxy ester type activated ester chemistry possesses intrinsic advantages over other click type reactions: (1) no catalyst for the post-polymerization process is required, ensuring a high tolerance toward other coexisting functional groups, (2) structural diversity of the benzene ring providing a variability in solubility and reactivity, and (3) ease of chemical modification on benzene ring of phenoxy ester type activated ester because of their chemical stability other than nucleophiles. The rational requirement for stimuli-triggered reactivity switching of activated ester based on phenoxy ester type activated ester would be a switching from an electron deficient leaving group to an electron-rich leaving group triggered by external stimuli. In order to meet this

Received: September 26, 2011
Revised: January 6, 2012
Published: January 31, 2012

   dx.doi.org/10.1021/ma202175z | *Macromolecules* 2012, 45, 1331−1338

Scheme 1. Schematic Representation of Temperature-Triggered Reactivity On−Off Switching of an Activated Ester Functionality Embedded in Poly(4-acryloxyphenyldimethylsulfonium triflate)



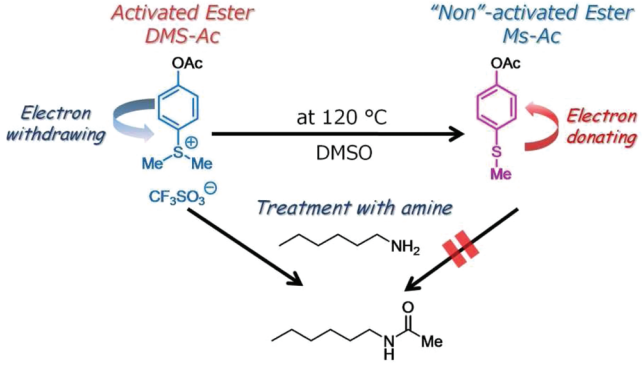
requirement, we turned our attention to the 4-dialkylsulfonium phenol as a stimuli-responsive leaving group.[29] First, 4-dialkylsulfonium phenol itself possesses highly acidic phenol proton with a $pK_a \approx 7.5$ and hence represents a good leaving group within ester derivatives because of the strong electron-withdrawing nature of sulfonium cation.[29] In addition, 4-dialkylsulfonium phenol is well-known to be decomposed applying a temperature stimuli to yield 4-alkylthiophenol, with a $pK_a \approx 10.0$, and hence its leaving-group ability of the respective ester derivatives is dramatically decreased because of electron-donating nature of the alkyl sulfide group.[29] In fact, Nagai and co-workers showed that incorporation of 4-dialkylsulfonium phenoxy ester moieties within a polymeric micelle exhibited a facile reactive site toward amines.[30−34] Furthermore, 4-acryloxyphenyldimethylsulfonium ion was revealed to possess facile radical polymerizability under both free and controlled radical polymerization conditions.[35−39] On the other hand, to the best of our knowledge, no detailed characterization about activated ester reactivity was yet reported for well-defined homopolymers featuring 4-dialkylsulfonium phenoxy ester moieties. In addition, a stimuli-triggered reactivity change of a 4-dialkylsulfonium phenoxy ester moiety within polymers has also never been examined.

Hence, in this article, we describe (i) the evaluation of our concept of external-stimuli triggered reactivity switching of 4-dialkylsulfonium phenoxy esters by means of model compounds and reactions, (ii) the RAFT polymerization of the corresponding monomer 4-acryloxyphenyldimethylsulfonium triflate to afford a polymeric activated ester, and (iii) the investigation of the post-polymerization modifications taking advantage of the switching behavior of the reactivity (Scheme 1).

RESULTS AND DISCUSSION

Monomer Design Concept of Stimuli-Responsive Activated Ester Monomer (SR-AEM). The monomer design concept in this article is comprised of the following two points: (1) a structural change of the leaving group from an electron-withdrawing state to an electron-donating group triggered by a temperature stimuli and (2) the reactivity change in the ester linkage along with the structural change in leaving group. To meet these requirements, 4-(dimethylsulfonium)phenol was selected as stimuli-responsive leaving group. First, model reactive compounds using the 4-acetoxyphenyldimethylsulfonium triflate (DMS-Ac) as an activated ester form and 4-(methysulfide)-phenoxy acetate (MS-Ac) as the corresponding deactivated ester were investigated to confirm whether the concept of reactivity change properly works or not (see Scheme 2). In order to provide

Scheme 2. Schematic Representation of Temperature-Triggered Reactivity On−Off Switching in Activated Ester Functionality for Model Compounds



a direct evidence of the structural change of the sulfonium ion group triggered by temperature, the reaction of DMS-Ac during heating was directly monitored by ^{1}H NMR. The thermal reaction of DMS-Ac was conducted in DMSO by heating to 120 °C for 1 h. As shown in Figure 1, the thermal treatment induced distinct structural changes and the observed ^{1}H NMR signals are in a perfect agreement with the peaks observed for the corresponding MS-Ac as the deactivated ester compound. To investigate the reactivity change, the model reactions between the model compounds MS-Ac or DMS-Ac with hexylamine were also directly monitored by ^{1}H NMR. As a direct consequence of the electron-donating nature of the methyl sulfide group, the deactivated ester of MS-Ac showed 0% conversion even after 1 h in the presence of 2.0 equiv of hexylamine (see Figure S-1, Supporting Information). By design, this is in a clear contrast to the results that had been obtained for the reaction of DMS-Ac in the presence of just 1.1 equiv of hexylamine. Because of the introduction of the

dx.doi.org/10.1021/ma202175z | Macromolecules 2012, 45, 1331−1338

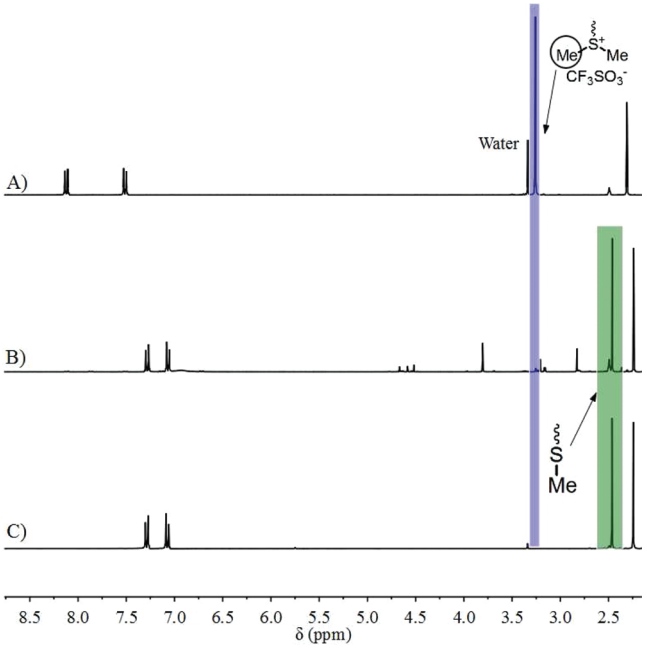


Figure 1. ^{1}H NMR spectra in DMSO-d_6 of (A) DMS-Ac, (B) DMS-Ac after thermal treatment at 120 °C in DMSO-d_6 for 1 h without purification, and (C) MS-Ac.

sulfonium ion group at the para position in the benzene ring, a drastic reactivity change was induced, resulting in over 95% conversion within 40 min (see Figure 2A). Because

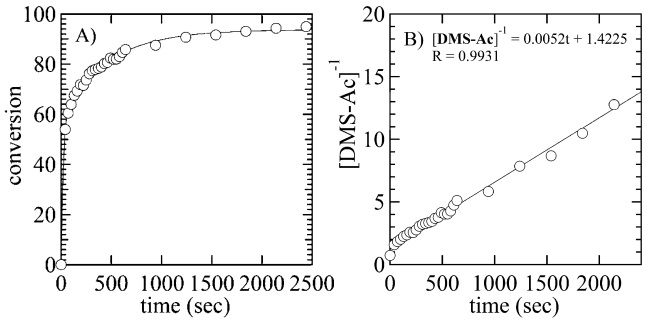


Figure 2. (A) Conversion of the DMS-Ac for the reaction between DMS-Ac and hexylamine in $CDCl_3$ (line; guidance). (B) Kinetic plots for the reaction between DMS-Ac and hexylamine in $CDCl_3$.

trialkylsulfonium ions are well-known to act as methylating agent for nucleophiles, which might cause potential side reactions, IR measurements of the reaction system were conducted to provide a direct evidence that the amidation reaction indeed took place at the carbonyl group (Figure 3). To be more precise, in the FT-IR spectrum of the DMS-Ac after reaction with hexylamine (Figure 3A) a distinct band at 1653 cm^{-1} owing to the C═O stretch of amide group developed while the band at 1763 cm^{-1} owing to the C═O stretch of activated ester group disappeared. Thus, the amidation reaction of DMS-Ac indeed took place at the carbonyl group. Furthermore, a kinetic study for the model reaction between DMS-Ac and hexylamine revealed a very fast amidation reaction at 25 °C and followed a second-order kinetic nature, which is consistent with the two component reaction of DMS-Ac with hexylamine (Figure 2). Thus, these model reactions supported that the main concept of thermally induced reactivity change can be achieved by using

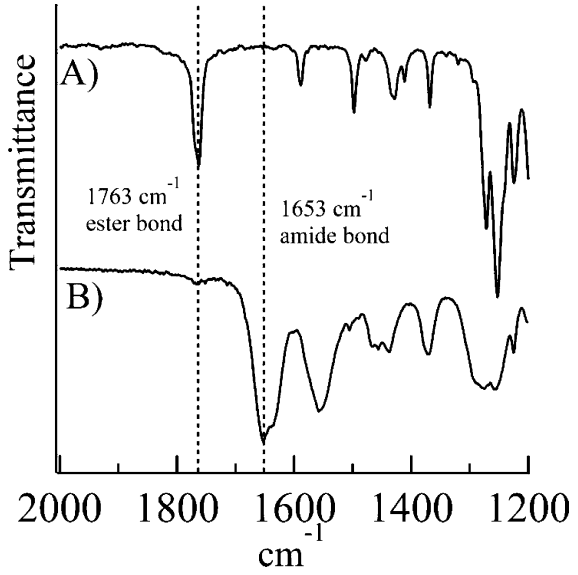


Figure 3. IR spectra of the DMS-Ac before (A) and after (B) the reaction with hexylamine in $CHCl_3$.

4-(dimethylsulfonium)phenol triflate as a thermoresponsive leaving group.

RAFT Polymerization of Stimuli-Responsive Activated Ester Monomer (SR-AEM). In order to realize the RAFT polymerization of 4-acryloxyphenyldimethylsulfonium triflate (SR-AEM), the synthetic procedure to obtain SR-AEM followed general design principles based on a methodology employed by Huck et al.[35] Briefly, 4-methylsulfide phenoxy acrylate, obtained by standard esterification chemsitry of 4-methylsulfide phenol with acryloyl chloride, was reacted with methyl triflate (MeOTf). The key step was the methylation of the sulfide linkage using MeOTf, which avoided the possibility of metal contamination and hence shows high compatibility with RAFT technique. Next, we carried out the RAFT polymerization of SR-AEM using pentafluorophenyl-(4-phenyl-thiocarbonylthio-4-cyanovalerate) as the chain transfer agent (PFP-CTA) and AIBN as a radical source in acetonitrile at 90 °C under an argon atmosphere with a ratio of $[SR\text{-}AEM]_0/[PFP\text{-}CTA]_0/[AIBN]_0$ being 50:1:0.5.[40] The SR-AEM monomer conversion reached 86% after 2 h, yielding poly(SR-AEM) with a degree of polymerization (DP_{NMR}) of 50.4 and a molecular weight distribution (M_w/M_n) of 1.32 in 70% isolated yield. The degree of polymerization of the obtained poly(SR-AEM) (DP = 50.4) was in good agreement with theoretical $DP_{theoretical}$ = 43.1, which was calculated from the initial ratio of $[SR\text{-}AEM]_0/[PFP\text{-}CTA]_0$. In addition, the SEC curve of the obtained polymer was unimodal, and its M_w/M_n value was fairly narrow,[41] indicating that the polymerization occurred in a controlled fashion. In the ^{1}H NMR spectrum of the obtained polymer, the major signals in the range both from 7.2 to 7.6 ppm and from 7.9 to 8.2 ppm were assigned to the aromatic protons and the sharp singlet signal in the range from 3.0 to 3.3 ppm was assigned to the methyl protons of disulfonium ion moiety, while the remaining broad signals appearing in the range from 1.9 to 2.5 ppm were assigned to the protons of the polyacrylate backbone (see Figure 4, upper spectrum). Thus, these results indicated that the RAFT polymerization of SR-AEM proceeded in a controlled manner with fairly good control over polymerization yielding poly(SR-AEM).

dx.doi.org/10.1021/ma202175z | Macromolecules 2012, 45, 1331−1338

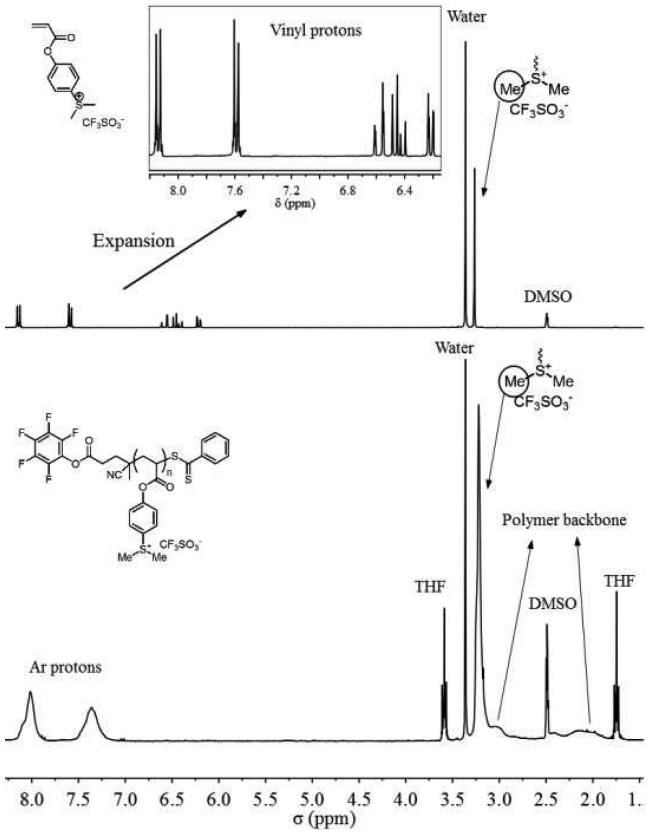


Figure 4. ^{1}H NMR spectra of the SR-AEM (upper) and poly(SR-AEM) (lower) in DMSO-d_6.

To confirm that the polymerization system proceeded in a controlled fashion, we carried out the RAFT polymerization of SR-AEM using various ratios of the $[SR\text{-}AEM]_0/[PFP\text{-}CTA]_0$ from 20 to 80 (Table 1 shows the polymerization results). As a direct consequence of the living nature of the RAFT polymerization of SR-AEM, the obtained poly(SR-AEM) had molecular weights that matched the theoretical values calculated by the $[SR\text{-}AEM]_0/[PFP\text{-}CTA]_0$ (SEC traces of runs 1, 8, and 9 in Table 1 are shown in Figure 5). It turned out, however, that a better control was obtained for smaller ratios of

Table 1. RAFT Polymerization of SR-AEM Using PFP-CTA as Chain Transfer Agent[a]

run	$[M]_0/[CTA]_0/[AIBN]_0$	time (min)	conv[b] (%)	DP_{theo}[c]	DP_{NMR}[d]	M_w/M_n[e]
1	50/1/0.5	120	86.2	43.1	48.8	1.32
2	50/1/0.5	20	0	n.d.	n.d.	n.d.
3	50/1/0.5	30	17.0	8.5	8.7	1.18
4	50/1/0.5	40	45.0	22.5	28.9	1.17
5	50/1/0.5	50	64.3	32.2	30.0	1.18
6	50/1/0.5	60	79.4	39.7	41.3	1.30
7	50/1/0.5	90	81.3	40.7	48.8	1.28
8	20/1/0.5	120	90.5	18.1	18.6	1.17
9	80/1/0.5	120	90.2	73.6	65.5	1.44

[a][M] = 0.93 mol L^{-1}; solvent, CH_3CN; temperature, 90 °C. [b]Determined by ^{1}H NMR in $CDCl_3$. [c]Calculated from $([M]_0/[I]_0) \times$ conv. [d]Determined by end-group analysis using ^{19}F NMR in DMSO-d_6. [e]Determined by SEC in THF using PSt standards. The poly(SR-AEM)s were thermally treated prior to injection to the SEC7.

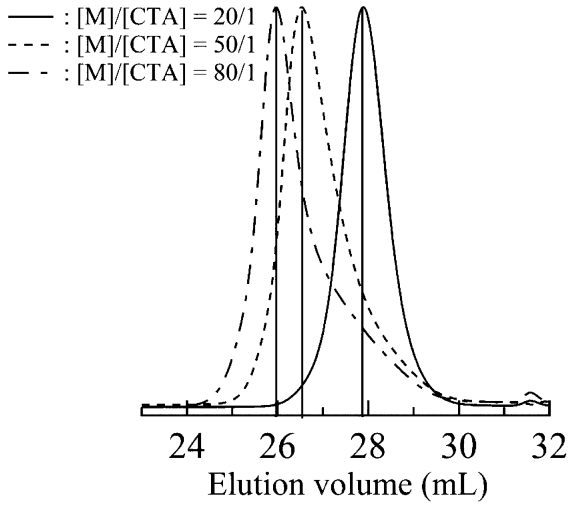


Figure 5. SEC traces of the poly(SR-AEM) (runs 1, 8, and 9; eluent, THF; flow rate, 1.0 mL min^{-1}). The poly(SR-AEM)s were thermally treated prior to injection to the SEC.

$[SR\text{-}AEM]_0$ to $[PFP\text{-}CTA]_0$ as SEC revealed a slight tailing for the ratio of 80:1. For further evidence of the controlled nature of the RAFT polymerization of SR-AEM, we carried out a kinetic investigation in acetonitrile at 90 °C under an argon atmosphere with a ratio of $[SR\text{-}AEM]_0/[PFP\text{-}CTA]_0/[AIBN]_0$ being 50:1:0.5. Although a short induction period was observed, the kinetic experiments showed a distinct first-order relationship between the reaction time and monomer conversion until the polymerization system reached around 80% monomer conversion (Figure 6A). Furthermore, the molecular weight of the obtained poly(SR-AEM) increased linearly with the reaction time (Figure 6B). It thus can be concluded that SR-AEM can be polymerized with a good control to molecular weights up to 25 kg/mol, making a very suitable candidate for a further investigation in post-polymerization modifications.

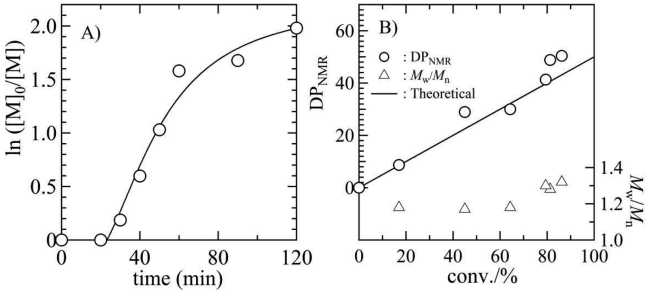


Figure 6. (A) Kinetic plots for the polymerization of SR-AEM (line; guidance). (B) Dependence of degree of polymerization (DP_{NMR}) and polydispersity (M_w/M_n) on the monomer conversion.

On−Off Reactivity Switching of the Activated Ester Moiety Embedded in Poly(SR-AEM). As a direct consequence of the successfully demonstrated preliminary model study (vide supra), the obtained poly(SR-AEM) was rationally expected to show a stimuli-responsive switching of its activated ester moiety. Hence, to verify the presence of the activated ester, the obtained polymer was reacted with an excess amount of *i*-Pr-NH_2 in CH_3CN for 19 h. After the reaction mixture was purified by dialysis in MeOH, a polymer powder was obtained in more than 83% isolated yield. The FT-IR spectrum of the obtained polymer revealed the development of a distinct band

dx.doi.org/10.1021/ma202175z | Macromolecules 2012, 45, 1331−1338

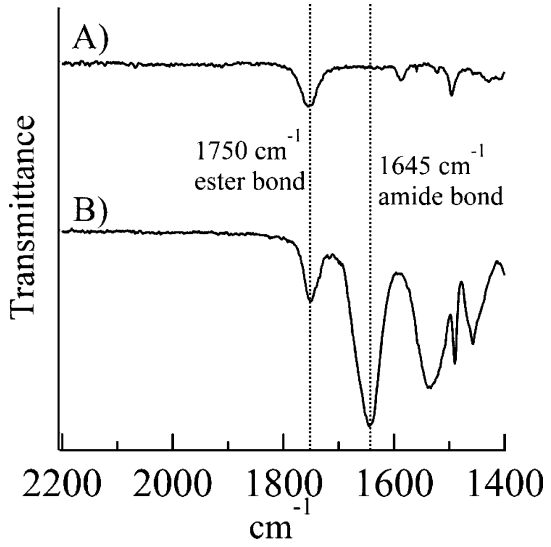


Figure 7. FT-IR spectra (ATR mode) of the poly(SR-AEM) before (A) and after (B) the reaction with *i*-Pr-NH_2 in CH_3CN.

at 1645 cm^{-1} owing to C═O stretch of amide group, while C═O stretch band of the activated ester group at 1750 cm^{-1} decreased dramatically (see Figure 7). Furthermore, in the ^1H NMR spectrum of the obtained polymer, distinct peaks due to isopropyl group appeared from 0.8 to 1.1 ppm and from 3.7 to 4.0 ppm while the peaks in the range from 7.1 to 7.6 ppm and from 7.8 to 8.2 ppm owing to the activated ester moiety disappeared (see Figure 8). Additionally, the ^1H NMR spectrum of the obtained polymer was in a good agreement with that of poly(*N*-isopropylacrylamide) synthesized by direct RAFT polymerization of *N*-isopropylacrylamide (see Figure 8B,C). The ^1H NMR spectrum of the obtained polymer revealed small but distinct peaks from 2.4 to 2.5 ppm owing to methyl sulfide linkage, showing that side reaction of methylating of amine took place in minor ratio of not more than 16%, based on ^1H NMR integration. The post-polymerization reaction took place predominantly with high efficiency. Thus, these results supported that the reaction between poly(SR-AEM) and *i*-Pr-NH_2 proceeded with high conversion affording poly(*N*-isopropylacrylamide) as a product, which showed that poly(SR-AEM) acted as a facile polymeric activated ester very similar to poly(*N*-succinimidyl acrylate) or poly(pentafluorophenyl acrylate).[16]

We next focused on the external stimuli responsive property of poly(SR-AEM). The thermal reaction of poly(SR-AEM) was conducted in DMSO at 120 °C, and the reaction progress was directly monitored by ^1H NMR measurement. As successfully demonstrated by the model reaction, poly(SR-AEM) was converted by thermo-triggered release of methyl group at dimethylsulfonium ion group to afford poly(4-acryloxyphenyl methylsulfide) (poly(APM)) as a nonactive form of poly(SR-AEM), which was directly proven by ^1H NMR measurement (see Figure 9). The signals in the ranges from 7.1 to 7.6 ppm and from 7.8 to 8.2 ppm due to phenyl ring bearing dimethylsulfonium ion group were completely shifted to the signal in the range from 6.8 to 7.3 ppm. In addition, the sharp peak in the range from 3.1 to 3.3 ppm owing to dimethylsulfonium ion group disappeared completely while a new peak appeared in the range from 2.4 to 2.5 owing to methylthio group. Furthermore, the ^1H NMR spectrum of the decomposed

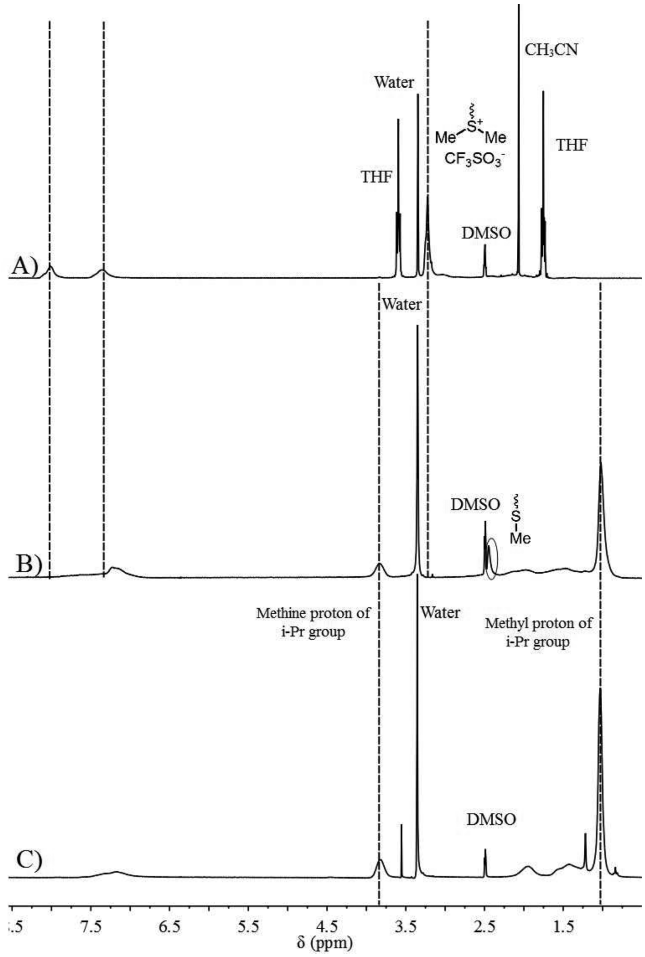


Figure 8. ^1H NMR spectra in DMSO-d_6 of (A) poly(SR-AEM), (B) poly(SR-AEM) after the treatment with *i*-Pr-NH_2 in CH_3CN overnight, and (C) poly(*N*-isopropylacrylamide) synthesized by radical polymerization.

polymer by thermo-reaction was in perfect agreement with the ^1H NMR spectrum of poly(4-methylthiophenoxy acrylate), which was prepared by direct RAFT polymerization of 4-methylthiopheoxy acrylate (see Figure 9). In addition to the spectral evidence, the solubility of the decomposed polymer differed from poly(SR-AEM). As a direct consequence of the highly ionic nature of poly(SR-AEM), poly(SR-AEM) showed a good solubility in only polar solvents such as MeOH, DMSO, DMF, and acetonitrile while it was insolubile in THF or $CHCl_3$. In a clear contrast, the nonactive form of poly(SR-AEM) was only soluble in nonpolar solvents such as THF, $CHCl_3$, CH_2Cl_2, and 1,4-dioxane, which strongly supported that the obtained polymer lost its ionic nature and thus its activated ester behavior during the decomposition. Thus, it turned out to be very clear that poly(SR-AEM) was converted to poly(4-methylthiophenoxy acrylate) by the temperature-triggered reaction, which also resulted in a solubility change from an even water-soluble polymer to nonpolar polymer by a simple thermal treatment.

We finally focused on the examination of on−off reactivity switching in poly(SR-AEM) triggered by the temperature stimulus. We evaluated the reactivity for both poly(SR-AEM) and poly(APM) using 1.1 equiv of various amines in CD_3CN and $CDCl_3$, respectively, for 1 h at room temperature, and the reactions were directly monitored by ^1H NMR measurements. It has to be noted that longer reaction times will lead in

dx.doi.org/10.1021/ma202175z | *Macromolecules* 2012, 45, 1331−1338

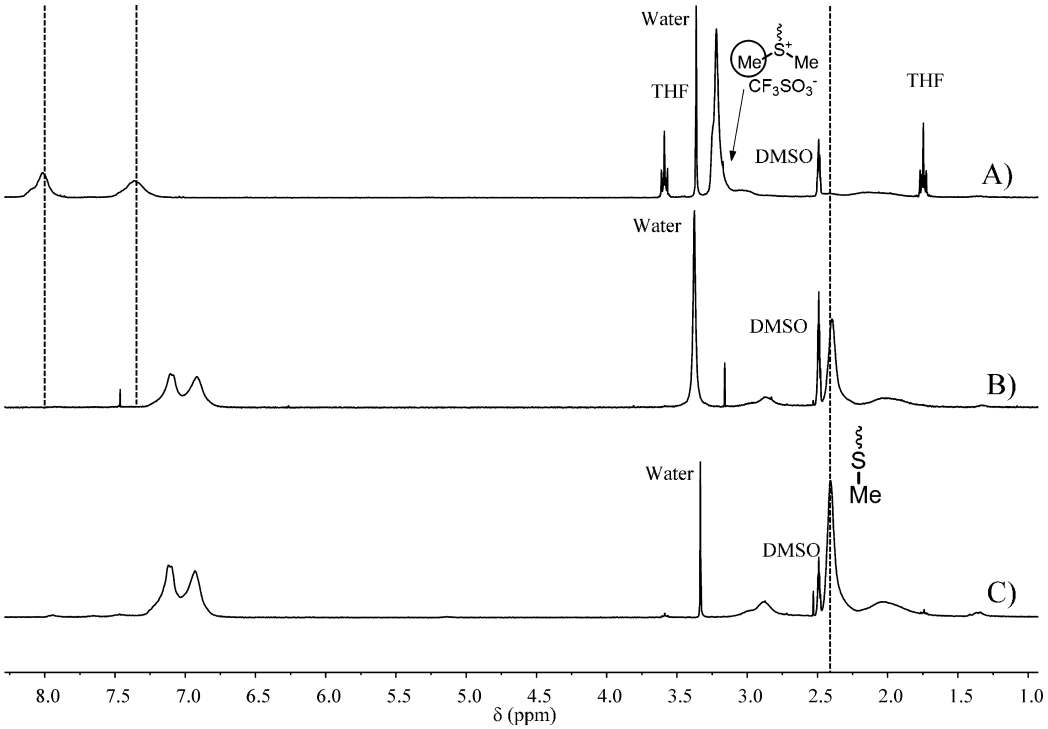


Figure 9. ^{1}H NMR spectra in DMSO-d_6 of (A) poly(SR-AEM), (B) poly(SR-AEM) after thermal treatment at 120 °C in DMSO overnight, and (C) poly(APM) synthesized by RAFT polymerization of 4-acryloxyphenyl methylsulfide.

particular for the reactive poly(SR-AEM) to higher conversions. However, to obtain comparable data, reaction times of 1 h were chosen. As shown in Figure 10, poly(SR-AEM) reacted with

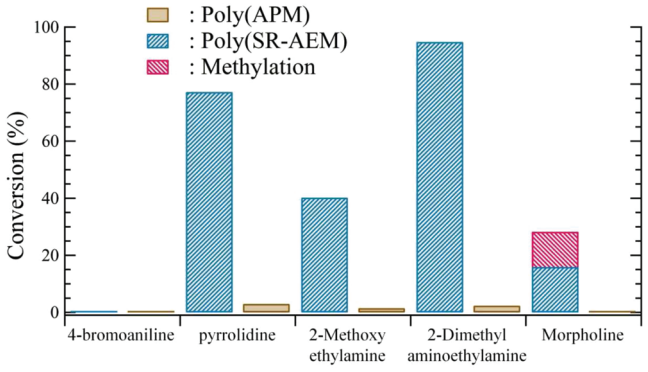


Figure 10. Reactivity comparison of poly(SR-AEM) with poly(APM) using various amines.

various amines except for aromatic amines, such as aniline. This reactivity tendency is similar to that of poly(pentafluorophenyl acrylate).[21] Thus, poly(SR-AEM) can be referred to the "on" state with respect to reactivity. On the other hand, the non-active form of poly(SR-AEM), mainly poly(APM), which was obtained after decomposition of poly(SR-AEM), showed a dramatically decreased reactivity toward various amines including even primary amines which are known to show high reactivity toward activated ester such as pentafluorophenyl ester.[21] When morpholine was used, the side reaction of methylation reaction was also observed as in the case of isopropylamine. Because of high vapor pressure of isopropylamine, it was not used in this comparative study; however, isopropylamine can successfully be used in the post-functionalization reaction for the post-modification of poly(SR-AEM) (vide supra). Interestingly, 2-methoxyethylamine showed a relatively low conversion of only 40% after 1 h. In contrast, the experiments with pyrrolidine and 2-dimethylaminoethylamine showed very high conversions of the activated ester poly(SR-AEM) after 1 h (77% and 94%, respectively), while almost no conversion of the deactivated poly(APM) could be observed.[42] This result clearly showed that decomposed state of poly(SR-AEM) can be termed as "off" state with respect to reactivity. Accordingly, this study represents the first example of a stimuli-triggered "on–off" switching in reactivity of an activated ester by utilizing 4-dimethylsulfonim phenol as stimuli-responsive leaving group.

■ CONCLUSIONS

In this study, we succeeded in the establishment of a new concept of external-stimuli triggered reactivity switching in phenoxy ester type click reaction using 4-dialkylsulfonium phenol as stimuli-responsive leaving group. The successful concept was demonstrated by means of model compounds and reactions. In addition, the RAFT polymerization of 4-acryloxyphenyldimethylsulfonium triflate was achieved using PFP-CTA as chain transfer agent affording polymeric activated ester of poly(SR-AEM) with good control over the polymerization. Obtained poly(SR-AEM) was successfully converted to deactivated ester state of poly(APM) by heating, i.e., stimulation by temperature. To the best of our knowledge, we realized the first temperature induced "on–off" switching in reactivity of activated ester by using 4-dimethylsulfonium phenol as stimuli-responsive leaving group.

■ EXPERIMENTAL SECTION

Materials. The methyltriflate was available from the Sigma-Aldrich Chemicals Co. and used as received. The 4-(methylthio)phenol was purchased from the Tokyo Kasei Kogyo Co., Ltd., and used as received. For polymerization, HPLC grade acetonitrile (>99.9%) was purchased from the VWR Co., Inc., and used without further

dx.doi.org/10.1021/ma202175z | Macromolecules 2012, 45, 1331–1338

purification. The pentafluorophenyl-(4-phenylthiocarbonylthio-4-cyanovalerate) was synthesized according to a previous report.[38] All other chemicals were commercially available and used without further purification unless otherwise stated.

Instruments. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deuterated solvents and chemical shifts (δ) were given in ppm as solvent peak as internal standard. ^{19}F NMR spectra were recorded on a Bruker 400 MHz FT-NMR spectrometer in deuterated solvents. The size exclusion chromatography (SEC) was performed at room temperature using a Jasco high performance liquid chromatography (HPLC) system (PU-1580 Intelligent HPLC pump, RI-1530 Intelligent RI detector, AS-1555 Intelligent HPLC autosampler, and DG-2080-53 degasser) equipped with three MZ Analysetechnik MZ-Gel SDplus columns in THF at a flow rate of 1.0 mL min^{-1}. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer using an ATR unit.

Synthesis of Stimuli-Responsive Activated Ester Monomer. *Synthesis of 4-Acryloxyphenyl Methylsulfide.* To the CH_2Cl_2 solution (30 mL) of 4-methylsulfide phenol (10.0 g, 71.4 mmol) and triethylamine (7.96 g, 78.6 mmol) was added acryloyl chloride (7.12 g, 78.6 mmol) in CH_2Cl_2 (20 mL) at 0 °C for 30 min. After the reaction mixture was stirred at room temperature overnight, the mixture was filtered. The filtrate was collected and washed with 1 N HCl(aq), 1 N Na_2CO_3(aq), and water. The organic layer was dried with $MgSO_4$. The solution was evaporated to give 4-acryloxyphenyl methylsulfide as pale brown liquid. Yield: 11.3 g (58.2 mmol, 81.5%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.26 (2H, d, J = 8.9 Hz), 7.05 (2H, d, J = 8.9 Hz), 6.58 (1H, dd, J = 17.3, 1.3 Hz), 6.29 (1H, dd, J = 17.3, 10.4 Hz), 5.98 (1H, dd, J = 10.4, 1.3 Hz), 2.45 (3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 164.50, 148.27, 135.72, 132.64, 127.96, 127.81, 121.97, 16.44.

Synthesis of 4-Acryloxyphenyldimethylsulfonium Triflate (SR-AEM). To a CH_2Cl_2/CH_3CN mixture solution (40/4 mL) of 4-methylsulfide phenoxy acrylate (8.0 g, 41.2 mmol) methyl triflate (7.4 g, 45.2 mmol) was slowly added at 40 °C and allowed to react for 16 h. Afterward, the reaction mixture was cooled down to room temperature, and the mixture was poured into large portion of diethyl ether. The precipitate was collected and dissolved in hot THF. The THF solution was poured into large portion of diethyl ether to yield 4-acryloxyphenyldimethylsulfonium triflate as pale yellow solid. Yield: 14.6 g (40.7 mmol, 98.8%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 8.14 (2H, d, J = 8.9 Hz), 7.59 (2H, d, J = 8.9 Hz), 6.58 (1H, dd, J = 17.2, 1.5 Hz), 6.44 (1H, dd, J = 17.2, 10.1 Hz), 6.21 (1H, dd, J = 10.1, 1.5 Hz), 3.27 (3H, s). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm): 163.75, 154.18, 134.68, 131.85, 127.26, 124.14, 123.98, 120.79 (q, J = 322.2 Hz), 28.47. ^{19}F NMR (DMSO-d_6) δ (ppm): −78.1 (3F, s). FT-IR (ATR-mode): 1739 cm^{-1} (C═O reactive ester band) Anal. Calcd for $C_{12}H_{13}F_3O_5S_2$ (358.35): C, 40.22; H, 3.66. Found: C, 40.09; H, 3.57.

General Procedure for RAFT Polymerization of SR-AEM. RAFT polymerization of SR-AEM was carried out as follows: An acetonitrile solution (1.5 mL) containing SR-AEM (500 mg, 1.4 mmol), pentafluorophenyl-(4-phenylthiocarbonylthio-4-cyanovalerate) (12.5 mg, 0.028 mmol), and AIBN (2.3 mg, 0.014 mmol) was degassed with Ar at room temperature for 15 min. After degassing, the reaction mixture was stirred at 90 °C for 2 h. The reaction mixture was then cooled down and exposed to air to quench the polymerization. A portion of the reaction mixture was collected for the purpose to determine the monomer conversion, while the rest of the reaction mixture was diluted with acetonitrile. The polymer was purified by reprecipitation (acetonitrile/THF) to produce pale red solid. Yield: 368 mg (73.6%).

Synthesis of Model Compounds. *Synthesis of 4-Acetoxyphenyl Methylsulfide (MS-Ac).* To a CH_2Cl_2 solution (15 mL) of 4-methylsulfide phenol (5.0 g, 35.7 mmol) and triethylamine (3.98 g, 39.3 mmol) acetyl chloride (7.12 g, 39.3 mmol) in CH_2Cl_2 (10 mL) was added at 0 °C for 30 min. After the reaction mixture was stirred at room temperature overnight, the mixture was filtered. The filtrate was collected and washed with 1 N HCl(aq), 1 N Na_2CO_3(aq), and water. The organic layer was dried with $MgSO_4$. The solution was evaporated to give 4-acetoxyphenyl methylsulfide as pale yellow solid. Yield: 5.9 g (32.6 mmol, 91.3%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.25 (d, J = 8.9 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 2.45 (s, 3H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 169.47, 148.37, 135.67, 127.97, 122.03, 21.07, 16.44.

Synthesis of 4-Acetoxyphenyldimethylsulfonium Triflate (DMS-Ac). To a CH_2Cl_2/CH_3CN mixture solution (10/1 mL) containing 4-acetoxyphenyl methylsulfide (2.0 g, 11.0 mmol) methyl triflate (2.0 g, 12.1 mmol) was slowly added at 40 °C and allowed to react for 13.5 h. Afterward, the reaction mixture was cooled down to room temperature, and the mixture was poured into large portion of diethyl ether. The precipitate was collected and dissolved in acetone. The acetone solution was poured into large portion of diethyl ether to yield 4-acetoxyphenyl dimethylsulfonium triflate as white powder. Yield: 3.3 g (9.5 mmol, 86.4%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 8.12 (2H, d, J = 8.8 Hz), 7.51 (2H, d, J = 8.8 Hz), 3.26 (6H, s), 2.31 (3H, s). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm): 168.91, 154.45, 131.79, 124.20, 123.71, 120.79 (q, J = 322.2 Hz), 28.48, 20.94. ^{19}F NMR (DMSO-d_6) δ (ppm): −78.1 (3F, s). FT-IR (ATR mode): 1763 cm^{-1} (C═O reactive ester band). Anal. Calcd for $C_{11}H_{13}F_3O_5S_2$ (346.34): C, 38.15; H, 3.78. Found: C, 37.86; H, 3.64.

Determination of Theoretical Degree of Polymerization for RAFT Polymerization. In a RAFT polymerization, a theoretical degree of polymerization was calculated as follows:

$$\mathrm{DP}_{\mathrm{theoretical}} = \frac{[\mathrm{monomer}]_0}{[\mathrm{CTA}]_0} \times (\mathrm{monomer\ conv})$$

The monomer conversion was directly determined from the ^{1}H NMR measurements of the polymerization mixtures.

SEC Measurements of the Polymers. Based on the fact that the obtained polymers are of highly ionic nature, the SEC measurement of the polymer was very difficult. Hence, the polymer was dissolved in DMSO and kept at 120 °C overnight in order to selectively decompose sulfonium ion structure in the polymer. The polymer solution was poured into large amount of MeOH. The obtained polymer was then used for SEC measurements in THF.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S-1. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel +49 (0) 40 42838 6009; Fax +49 (0) 40 42838 6008; e-mail theato@chemie.uni-hamburg.de.

■ ACKNOWLEDGMENTS

Ryohei Kakuchi gratefully acknowledges the support by a Grant-in-Aid for the Japan Society for the Promotion of Science (JSPS) Fellows.

■ REFERENCES

(1) Barner-Kowollik, C.; Du Prez, F. E.; Espeel, P.; Hawker, C. J.; Junkers, T.; Schlaad, H.; Van Camp, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 60−62.

(2) Becer, C. R.; Hoogenboom, R.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2009**, *48*, 4900−4908.

(3) Chu, C.; Liu, R. *Chem. Soc. Rev.* **2011**, *40*, 2177−2188.

(4) Fournier, D.; Hoogenboom, R.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1369−1380.

(5) Franc, G.; Kakkar, A. K. *Chem. Soc. Rev.* **2010**, *39*, 1536−1544.

(6) Fu, R.; Fu, G.-D. *Polym. Chem.* **2011**, *2*, 465−475.

(7) Golas, P. L.; Matyjaszewski, K. *Chem. Soc. Rev.* **2010**, *39*, 1338−1354.

(8) Hoyle, C. E.; Bowman, C. N. *Angew. Chem., Int. Ed.* **2010**, *49*, 1540−1573.
(9) Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. *Chem. Soc. Rev.* **2010**, *39*, 1355−1387.
(10) Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.* **2009**, *109*, 5620−5686.
(11) Lowe, A. B. *Polym. Chem* **2010**, *1*, 17−36.
(12) Lutz, J.-F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1018−1025.
(13) Qin, A.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **2010**, *43*, 8693−8702.
(14) Qin, A.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2010**, *39*, 2522−2544.
(15) Sumerlin, B. S.; Vogt, A. P. *Macromolecules* **2009**, *43*, 1−13.
(16) Theato, P. *J. Polym. Sci., Part A* **2008**, *46*, 6677−6687.
(17) Li, H.; Yu, B.; Matsushima, H.; Hoyle, C. E.; Lowe, A. B. *Macromolecules* **2009**, *42*, 6537−6542.
(18) Li, Q.; Zhou, H.; Wicks, D. A.; Hoyle, C. E.; Magers, D. H.; McAlexander, H. R. *Macromolecules* **2009**, *42*, 1824−1833.
(19) Biedermann, F.; Appel, E. A.; del Barrio, J.; Gruendling, T.; Barner-Kowollik, C.; Scherman, O. A. *Macromolecules* **2011**, *44*, 4828−4835.
(20) Ghosh, S.; Basu, S.; Thayumanavan, S. *Macromolecules* **2006**, *39*, 5595−5597.
(21) Nilles, K.; Theato, P. *J. Polym. Sci., Part A* **2010**, *48*, 3683−3692.
(22) Li, R. C.; Hwang, J.; Maynard, H. D. *Chem. Commun.* **2007**, 3631−3633.
(23) Malkoch, M.; Thibault, R. J.; Drockenmuller, E.; Messerschmidt, M.; Voit, B.; Russell, T. P.; Hawker, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 14942−14949.
(24) Yang, S. K.; Weck, M. *Macromolecules* **2007**, *41*, 346−351.
(25) Stuart, M. A. C.; Huck, W. T. S.; Genzer, J.; Muller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. *Nature Mater.* **2010**, *9*, 101−113.
(26) Klinger, D.; Chang, J. Y.; Theato, P. *Macromol. Rapid Commun.* **2007**, *28*, 718−724.
(27) Orski, S. V.; Poloukhtine, A. A.; Arumugam, S.; Mao, L.; Popik, V. V.; Locklin, J. *J. Am. Chem. Soc.* **2010**, *132*, 11024−11026.
(28) Jewett, J. C.; Bertozzi, C. R. *Chem. Soc. Rev.* **2010**, *39*, 1272−1279.
(29) Kouge, K.; Koizumi, T.; Okai, H.; Kato, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2409−2418.
(30) Nagai, K.; Ohashi, T.; Kaneko, R.; Taniguchi, T. *Colloids Surf., A* **1999**, *153*, 133−136.
(31) Takahashi, K.; Kido, J.; Kuramoto, N.; Nagai, K. *J. Colloid Interface Sci.* **1995**, *172*, 63−70.
(32) Takahashi, K.; Nagai, K. *Polymer* **1996**, *37*, 1257−1266.
(33) Takahashi, K.; Suzuki, M.; Kido, J.; Kuramoto, N.; Nagai, K. *Polymer* **1995**, *36*, 4675−4681.
(34) Yamaguchi, K.; Taniguchi, T.; Kawaguchi, S.; Nagai, K. *Colloid Polym. Sci.* **2002**, *280*, 942−948.
(35) Brown, A. A.; Azzaroni, O.; Fidalgo, L. M.; Huck, W. T. S. *Soft Matter* **2009**, *5*, 2738−2745.
(36) Kim, Y. J.; Kang, H.; Leolukman, M.; Nealey, P. F.; Gopalan, P. *Chem. Mater.* **2009**, *21*, 3030−3032.
(37) Wu, H.; Gonsalves, K. E. *Adv. Mater.* **2001**, *13*, 195−197.
(38) Wu, H.; Gonsalves, K. E. *Adv. Mater.* **2001**, *13*, 670−672.
(39) Wu, H.; Gonsalves, K. E. *Adv. Funct. Mater.* **2001**, *11*, 271−276.
(40) Although Gopalan et al. reported RAFT polymerization of 4-acryloxyphenyldimethylsulfonium triflate using 2-cyanoprop-2-yl dithiobenzoate as CTA and AIBN as radical source at 60 °C, the temperature of 90 °C was mandatory in this system. Please see ref 36.
(41) The poly(SR-AEM)s were thermally treated prior to injection to the SEC.
(42) The observed distinct discrepancy of poly(SR-AEM) reactivity toward amines might be owing to the differences in steric hindrance of utilized amines although the quantitative analysis about this reactivity discrepancy is necessary for further discussions.