# Syndiotactic specific radical polymerization of *N*-isopropylacrylamide in toluene at low temperatures in the presence of silyl alcohols

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**ABSTRACT:** The radical polymerization of *N*-isopropylacrylamide (NIPAAm) was carried out in toluene at low temperatures in the presence of silyl alcohols, such as triethylsilanol (TESiOH). Poly(NIPAAm) with a *racemo* dyad content of 75 % was

obtained at –80 °C with a 4:1 TESiOH to monomer ratio loading. NMR analysis has suggested that the mechanism for syndiotactic induction, in the presence of silyl alcohols, may be similar to that observed with alkyl alcohols. In this case, a 1:2 complex formation, via hydrogen bonding interactions, leads to the induction of syndiotactic specificity.

**INTRODUCTION**

The development of novel and facile methodologies for the preparation of stereoregular polymers attracts significant attention, since tacticity can affect the thermal, mechanical, and solution properties of polymers. Stereocontrol in radical polymerization is now achievable to a certain extent for a wide range of monomers via a range of strategies.[1-5] One of the strategies involves alcohol compounds, which form complexes with the monomers through hydrogen bonding interactions. This strategy has been used to

induce stereospecificity in the radical polymerization of vinyl monomers, such as vinyl esters,[6, 7] methacrylates,[8, 9] *N*-vinylamides,[10, 11] and acrylamides.[12-16]

Of these alcohol-mediated stereospecific radical polymerizations, the stereospecificity in the radical polymerization of *N*-isopropylacrylamide (NIPAAm) in toluene at low temperature was observed to exhibit a significant dependence on the type of alcohol added. For example, the addition of alkyl alcohols (ROH), such as *tert*-butyl alcohol (*t*-BuOH) or 3-methyl-3-pentanol (3Me3PenOH), leads to syndiotactic poly(NIPAAm)s,[12] whereas the addition of fluorinated alcohols (RfOH), such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) or nonafluoro-*tert*-butanol (NFTB), leads to heterotactic poly(NIPAAm)s.[14] NMR analysis of the monomer/alcohol mixtures suggests that differences in their respective hydrogen bonding complexes lead to the differences in induced stereospecificity (Scheme 1).
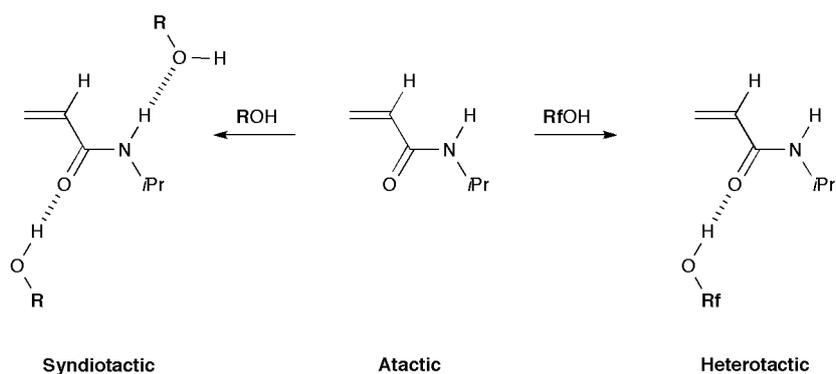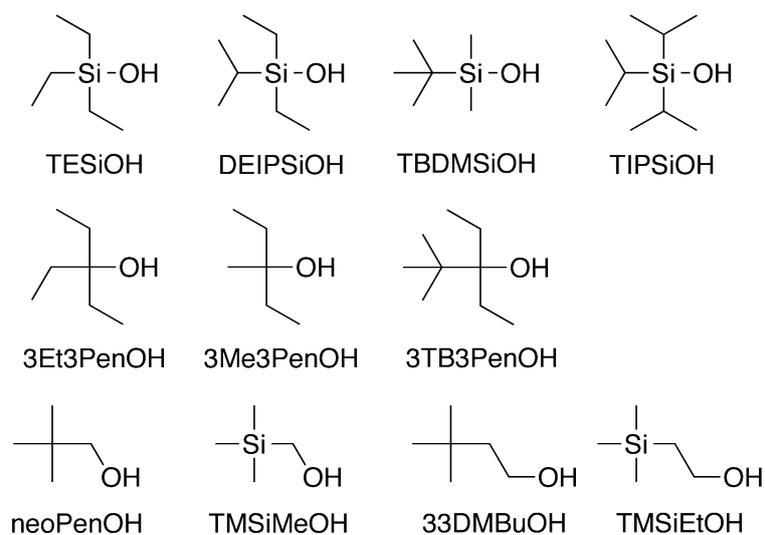
**Scheme 1.** Relationship between hydrogen bond complex structure and stereospecificity in NIPAAm polymerization.

Silyl alcohols, which are known to form hydrogen bonding interactions through their silanol groups (Si–OH),[17] have been extensively investigated as stable siloxane framework precursors.[18] A lithium salt of a silyl alcohol, lithium trimethylsilanolate (Me$_3$SiOLi), was used as an isotactic-specificity enhancer in the anionic polymerization of methyl methacrylate.[19] To the best of our knowledge, however, there have been no reports on the use of silyl alcohols as reagents to control stereospecificity in vinyl polymerizations. In this paper, the radical polymerization of NIPAAm was carried out in toluene at low temperatures in the presence of a silyl alcohol, to examine whether silyl alcohols can also induce stereospecificity.

**EXPERIMENTAL**

**Materials**

NIPAAm (Tokyo Chemical Industry Co., Ltd, Tokyo, Japan) was recrystallized from a hexane-toluene mixture. Toluene was purified by washing with sulfuric acid, water and 5% aqueous NaOH, followed by fractional distillation. Triethylsilanol (TESiOH), diethyl(isopropyl)silanol (DEIPSiOH), 3-ethyl-3-pentanol (3Et3PenOH), trimethylsilylmethanol (TMSiMeOH), 2-(trimethylsilyl)ethanol (TMSiEtOH) (Tokyo Chemical Industry Co., Ltd), *tert*-butyldimethylsilanol (TBDMSiOH), triisopropylsilanol (TIPSiOH), 3,3-dimethyl-1-butanol (33DMeBuOH), 3-*tert*-butyl-3-pentanol (3TB3PenOH), tri-*n*-butylborane (*n*-Bu$_3$B), purchased as a 1.0 M tetrahydrofuran (THF) solution, (Sigma-Aldrich Japan, Tokyo, Japan), and neopentanol (neoPenOH) (Wako Pure Chemical Industries, Osaka, Japan) were used as received without further purification.

TESiOH      DEIPSiOH      TBDMSiOH      TIPSiOH

3Et3PenOH      3Me3PenOH      3TB3PenOH

neoPenOH      TMSiMeOH      33DMBuOH      TMSiEtOH

**Polymerization**

The typical polymerization procedure is as follows; NIPAAm (0.314 g, 2.8 mmol) and TESiOH (1.48 g, 11.2 mmol) were dissolved in toluene to prepare a 5 mL solution (0.56 mol/L). A total of 4 mL of this solution was transferred to a glass ampoule and cooled at –40 °C. The polymerization was initiated via the addition of an $n$-Bu$_3$B solution (0.22 mL). After 24 h, the reaction was terminated using a solution of 2,6-di-*tert*-butyl-4-methylphenol in THF (0.5 mL, 1.0 M). The polymerization mixture was poured into diethyl ether (200 mL). The precipitated polymer was collected by filtration or centrifugation, and dried *in vacuo*. The polymer yield was determined gravimetrically.

**Measurements**

^{1}H and ^{13}C NMR spectra were measured using an EX-400 spectrometer (JEOL Ltd., Tokyo, Japan) operated at 400 MHz for ^{1}H and 100 MHz for [13]C. The dyad tacticity was determined from the ^{1}H NMR signals for the methylene groups in the main chain, in deuterated dimethyl sulfoxide (DMSO-$d_6$) at 150 °C. The ^{1}H and ^{13}C NMR spectra for the mixture of NIPAAm and TESiOH were measured in toluene-$d_8$ at –20 °C. The molecular weights and molecular weight distributions of the polymers were determined via size exclusion chromatography (SEC); chromatographs were calibrated with a range of polystyrene standards. SEC measurements were performed on an HLC 8220 chromatograph (Tosoh Corp., Tokyo, Japan) equipped with TSK gel columns (SuperHM-M (6.5 mm ID × 150 mm) and SuperHM-H (6.5 mm ID × 150 mm), Tosoh Corp.). Dimethylformamide, containing LiBr (10 mmol L$^{-1}$), was used as the eluent at 40 °C with a flow rate 0.35 mL min$^{-1}$. The initial polymer concentrations were 1.0 mg mL$^{-1}$.

## RESULTS AND DISCUSSION

**Radical Polymerization of NIPAAm in Toluene at –40 °C in the Presence of Silyl Alcohols or Their Alkyl Analogues**

Radical polymerizations of NIPAAm were carried out in toluene at –40 °C, in the presence and absence of a fourfold amount of silyl or alkyl alcohol (Table 1, runs 2, 3, 15-17 and 19-25). The silyl and alkyl alcohols induced syndiotactic specificity in the NIPAAm polymerization. A polymer with a *racemo* (*r*) dyad content of 73% was obtained using TESiOH, whereas $r = 68\%$ was obtained with 3Et3PenOH (Table 1, runs 3, 20). This suggests that the silyl alcohols induce syndiotacticity more selectivity than the isostructural alkyl alcohols. Having the trimethylsilyl group separated from the OH group with a methylene (Table 1, runs 22, 23) or ethylene group (Table 1, runs 24, 25) scarcely affected the induced syndiotactic specificity. Thus, it is proposed that the Si-OH group is important for an enhanced induction of syndiotactic specificity in the NIPAAm polymerization.

<Table 1>

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The $r$ dyad content in the polymers decreased slightly as the bulkiness of the silyl alcohols increased (Table 1, runs 3, 15-17), but decreased more significantly as the bulkiness of the alkyl alcohols increased (Table 1, runs 19-21). For example, a polymer with $r = 71\%$ was obtained with TBDMSiOH, but a polymer with $r = 61\%$ was obtained with 3TB3PenOH. This difference is believed to originate from the differences in covalent radius for Si and C. The covalent radius for Si is larger than that for C, so the steric hindrance around the OH group in the silyl alcohols would be reduced. Further details will be discussed in a later section.

The radical polymerization of NIPAAm, in the presence of TESiOH, was carried out at different temperatures (Table 1, runs 3-8). TESiOH was selected as it induced the highest syndiotactic specificity of all the silyl alcohols examined. Figure 1 presents the relationship between polymerization temperature and $r$ dyad content for the poly(NIPAAm) obtained in the presence of TESiOH. The $r$ dyad levels for poly(NIPAAm), prepared in the presence or absence of 3Me3PenOH, are also plotted, as its skeleton is similar in structure to that of TESiOH, and it also induced significant

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syndiotactic specificity. This was reported in the previous paper.[12] TESiOH induced

more highly syndiotactic specificity than 3Me3PenOH, regardless of the temperature.

The $r$ dyad content in the poly(NIPAAm) reached 75 % upon lowering the temperature

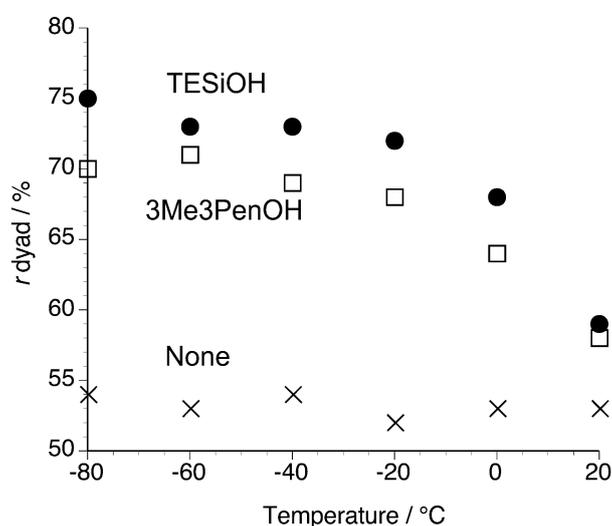to –80 °C (Figure 2), where the polymerization proceeded heterogeneously.



**Figure 1.** Relationship between polymerization temperature and $r$ dyad content for poly(NIPAAm)s prepared in toluene at low temperatures, in the presence or absence of TESiOH or 3Me3PenOH.
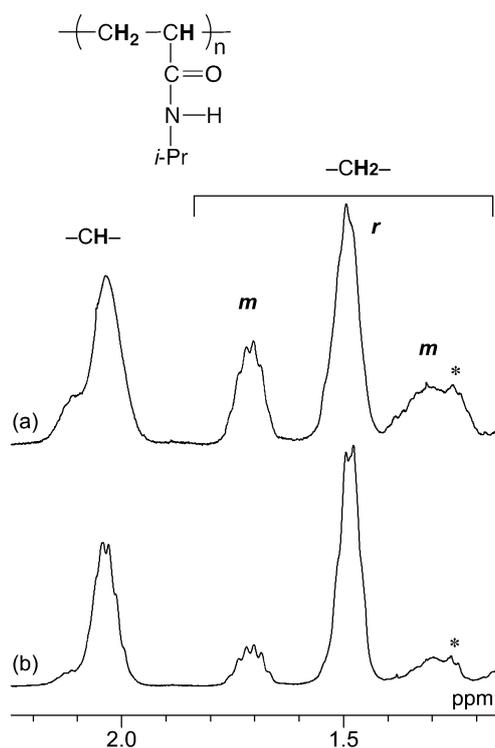
**Figure 2.** ^{1}H NMR spectra for the methylene and methine protons in the main chain of poly(NIPAAm)s prepared in toluene (a) at –40 °C in the absence of alcohols and (b) at –80 °C in the presence of TESiOH. The asterisk indicates the ^{13}C satellite peak of (C$H_3$)$_2$CH–.

The influence of TESiOH levels on the syndiotactic specificity was also investigated at –40 °C (Table 1, runs 3, 9-14).[20] Figure 3 shows the relationship between the [Alcohol]$_0$/[NIPAAm]$_0$ ratio and the *r* dyad content in the resulting polymers. The *r* dyad levels in the poly(NIPAAm)s, prepared in the presence of 3Me3PenOH, are also plotted.[12] No appreciable differences in induced syndiotactic specificity were observed

between TESiOH and 3Me3PenOH, when less than two equivalents of alcohol were employed. This suggests that the mechanisms for syndiotactic induction are similar for both silyl and alkyl alcohols. On the other hand, a slight improvement in syndiotactic specificity was observed in the presence of more than three equivalents of alcohol.



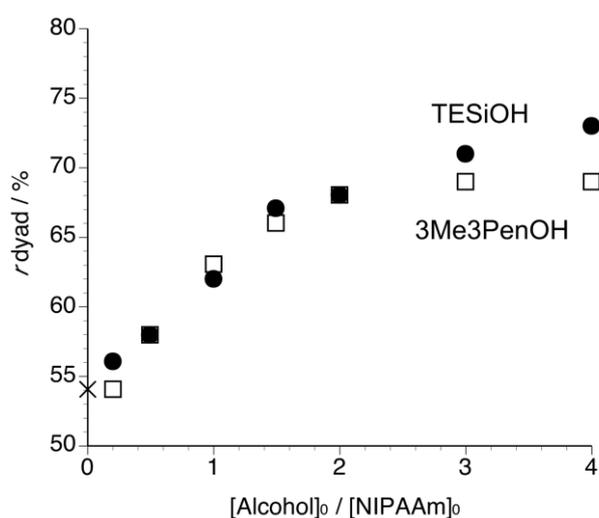**Figure 3.** Relationship between $[Alcohol]_0/[NIPAAm]_0$ ratio and $r$ dyad content for poly(NIPAAm)s prepared in toluene at $-40$ °C, in the presence or absence of TESiOH or 3Me3PenOH.

**Hydrogen-Bonding Interactions between the NIPAAm and Alcohol Components**

        To confirm the involvement of hydrogen bonding interactions in the stereocontrol of the NIPAAm polymerization, an NMR analysis was carried out on

mixtures of NIPAAm and TESiOH in toluene-$d_8$ at –20 °C. The concentration of

NIPAAm was kept at 0.2 mol $L^{-1}$. Even in the absence of NIPAAm monomer, the

chemical shift for the –OH proton of the TESiOH varied with concentration. This is

likely due to the self-association of TESiOH via hydrogen bonding interactions.[17] Thus,

the differences in chemical shift for the –OH proton of TESiOH [$\Delta\delta$(-OH)], in

comparison to a TESiOH control, were plotted against the $[Alcohol]_0/[NIPAAm]_0$ ratio,

as shown in Figure 4a. Figures 4b and 4c display the changes in the chemical shifts for

the –NH proton of the NIPAAm [$\Delta\delta$(-NH)] and the C=O carbon of NIPAAm [$\Delta\delta$(C=O)],

versus the $[Alcohol]_0/[NIPAAm]_0$ ratio, respectively. Data for NIPAAm and $t$-BuOH[12]

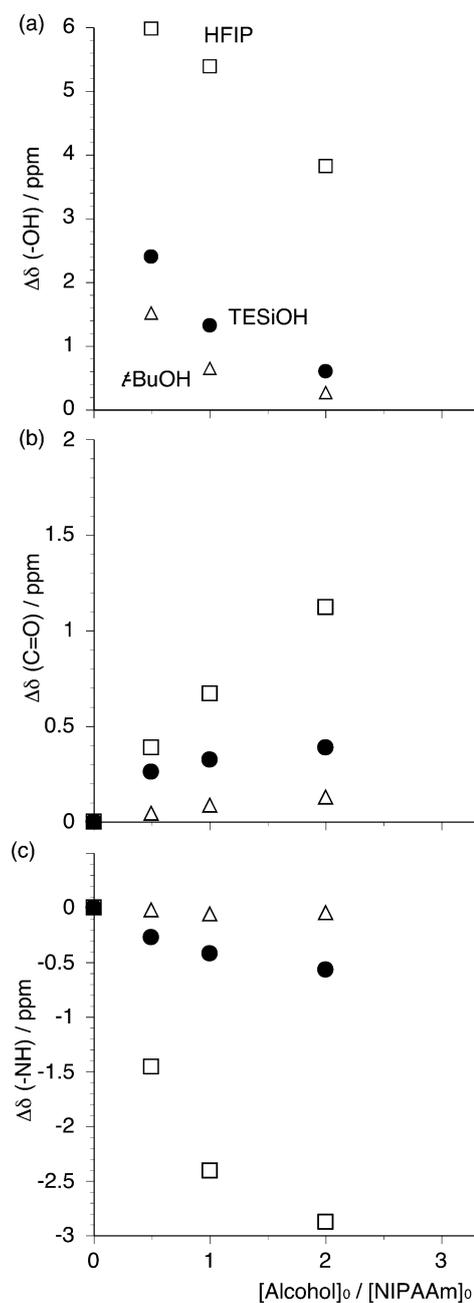(and HFIP) mixtures are also plotted in Figure 4.

**Figure 4.** (a) ^{1}H NMR chemical shift differences for the –OH protons of the alcohol, in the sample mixture and a control sample at corresponding concentrations, (b) changes in ^{13}C NMR chemical shift for the C=O carbons and (c) changes in ^{1}H NMR chemical shift for the –NH protons of NIPAAm monomer, as a function of the [Alcohol]$_0$/NIPAAm]$_0$ ratio.

The –OH signal for the TESiOH shows a downfield shift upon mixing with

NIPAAm, regardless of the TESiOH concentration (Figure 4a). The signal for the C=O

carbon in NIPAAm also exhibits a downfield shift, with increasing levels of TESiOH

(Figure 4b). These results suggest that the NIPAAm and TESiOH form a C=O•••H–O

hydrogen bonding interaction, as observed for alkyl and fluorinated alcohols.[12, 14] On

the other hand, the signal for the –NH proton in NIPAAm shows an upfield shift with

increasing TESiOH concentration. This upfield shift, however, is quite small compared

to that for HFIP (Figure 4c).

Fluorinated alcohols are acidic and exhibit a low basicity, due the inductive

effect of their fluorine atoms.[21-24] The signals for the C=O carbon and N–H proton of

NIPAAm exhibit large downfield and upfield shifts, respectively, with an increasing

concentration of fluorinated alcohol (Figures 4b and 4c). Thus, in a previous paper,[14] we

proposed a mechanism for the heterotactic radical polymerization of NIPAAm, in which

the NIPAAm monomer forms a 1:1 complex with the fluorinated alcohol via a

C=O•••H–O hydrogen bond (*cf*. Scheme 1).

Conversely, alkyl alcohols exhibit a lower acidity and a higher basicity

compared to fluorinated alcohols.[22, 23] Both the C=O carbon and N-H proton signals in NIPAAm exhibit downfield shifts in the presence of excess alkyl alcohol (Figures 4b and 4c). Thus, in a previous paper,[12] we proposed a mechanism for the syndiotactic radical polymerization of NIPAAm, in which NIPAAm monomer forms a 1:2 complex with the alkyl alcohol via O–H•••O=C–N–H•••O hydrogen bonding interactions (*cf.* Scheme 1), based on the cooperative effect.[25-27]

Silyl alcohols are nearly as basic as their corresponding alkyl alcohols, but are considerably more acidic, owing to their (p-d)π bonding, where the lone pairs of the oxygen overlap with the vacant silicon 3d orbitals.[28] TESiOH induces a syndiotactic specificity comparable to that with 3Me3PenOH, at addition levels up to two equivalents, as shown in Figure 3. Changes in the chemical shift for the mixtures of NIPAAm and TESiOH were small and comparable to those for NIPAAm and *t*-BuOH (*cf.* Figure 4). These results suggest that the silyl alcohols form a 1:2 complex with NIPAAm, as for the alkyl alcohols. It is this 1:2 complex formation that leads to the observed syndiotactic specificity.

In a previous paper,[12] we proposed that the coordination of the alkyl alcohol

to the N-H proton led to the induction of the syndiotactic specificity due to the steric

repulsion between the alcohols bound to the N-H groups at the propagating chain-end

monomeric unit, the penultimate monomeric unit and the incoming monomer. This was

because phosphoric acid derivatives also induce syndiotactic specificity in NIPAAm

polymerizations via coordination to the N-H proton.[29, 30] We propose that an analogous

coordination of the silyl alcohol to the N-H proton is responsible for the induction of

syndiotactic specificity in this present system. The steric repulsions between one

NIPAAm monomer and two alcohols are considered to inhibit complex formation as the

bulkiness of the alcohol increases. In fact, the syndiotactic specificity observed with

bulky alkyl alcohols is significantly reduced. However, TESiOH, which is bulkier than

3Me3PenOH, exhibits a slight improvement in the induced syndiotactic specificity. This

may be a result of decreased steric hindrance around the OH group, owing to the larger

covalent radius of Si *vs* C.

The basicities of the silyl and alkyl alcohols increase as they become involved

in self-association.[23, 31] Such an increase in basicity would promote their coordination to

N-H protons, and would also benefit from the cooperative effect.[25-27] However, the *r*

dyad content for polymers prepared in the presence of 3Me3PenOH began to plateau off

at $[\text{Alcohol}]_0/[\text{NIPAAm}]_0$ ratios over 3 (*cf.* Figure 3). This is probably due to the steric

repulsions that arise between the NIPAAm and 3Me3PenOH. On the other hand, the *r*

dyad levels for polymers prepared in the presence of TESiOH increased with increasing

TESiOH concentration (*cf.* Figure 3). We propose that the larger covalent radius for Si

than C allows the silyl alcohol to form a 1:2 complex more readily than the alkyl

alcohol. This results in an enhancement in syndiotactic specificity in the presence of

more than three equivalents of silyl alcohol.


**CONCLUSION**

The radical polymerization of NIPAAm has been investigated in toluene at low

temperatures, in the presence of silyl alcohols. Silyl alcohols act a useful reagent to

induce syndiotactic specificity, and silyl alcohols enforce a greater stereocontrol than

their corresponding alkyl alcohols. An NMR analysis has suggested that the mechanism

for this syndiotactic induction with silyl alcohols is similar to that observed with alkyl

alcohols, where a 1:2 hydrogen-bonding complex is key to specificity. The

improvements in syndiotactic specificity result from the structural features of the silyl alcohols. They have a high acidity, a basicity similar to the alkyl alcohols and a larger covalent radius in silicon compared to carbon.

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**Table 1.** Radical polymerization of NIPAAm in toluene for 24 h, in the presence or absence of silyl or alkyl alcohol[a]

| Run | Added alcohol | [Alcohol]$_0$ mol L$^{-1}$ | Temp. °C | Yield % | Dyad / %[b] m | r | $M_n$[c] × 10$^{-4}$ | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|---|---|
| 1[d] | None | 0.0 | 20 | 80 | 47 | 53 | 2.31 | 2.1 |
| 2[e,f] | None | 0.0 | −40 | 89 | 46 | 54 | 2.72 | 1.8 |
| 3 | TESiOH | 2.0 | −40 | >99 | 27 | 73 | 6.72 | 1.9 |
| 4[d] | TESiOH | 2.0 | 20 | 85 | 41 | 59 | 3.02 | 2.0 |
| 5 | TESiOH | 2.0 | 0 | 98 | 32 | 68 | 4.62 | 1.9 |
| 6 | TESiOH | 2.0 | −20 | 92 | 28 | 72 | 6.58 | 1.8 |
| 7[e] | TESiOH | 2.0 | −60 | >99 | 27 | 73 | 6.24 | 1.5 |
| 8[e] | TESiOH | 2.0 | −80 | 84 | 25 | 75 | 7.44 | 2.2 |
| 9[e] | TESiOH | 0.10 | −40 | 33 | 44 | 56 | 4.70 | 1.8 |
| 10[e] | TESiOH | 0.25 | −40 | 93 | 42 | 58 | 5.67 | 1.8 |
| 11 | TESiOH | 0.50 | −40 | 95 | 38 | 62 | 6.25 | 1.8 |
| 12 | TESiOH | 0.75 | −40 | 96 | 33 | 67 | 7.39 | 1.7 |
| 13 | TESiOH | 1.0 | −40 | 96 | 32 | 68 | 8.35 | 1.7 |
| 14 | TESiOH | 1.5 | −40 | 96 | 29 | 71 | 7.97 | 2.1 |
| 15 | DEIPSiOH | 2.0 | −40 | 93 | 28 | 72 | 6.11 | 1.7 |
| 16 | TBDMSiOH | 2.0 | −40 | >99 | 29 | 71 | 5.34 | 1.6 |
| 17 | TIPSiOH | 2.0 | −40 | 92 | 36 | 64 | 3.34 | 1.7 |
| 18[d] | 3Me3PenOH | 2.0 | 20 | 84 | 42 | 58 | 3.14 | 2.0 |
| 19[f] | 3Me3PenOH | 2.0 | −40 | >99 | 31 | 69 | 5.88 | 1.5 |
| 20 | 3Et3PenOH | 2.0 | −40 | >99 | 32 | 68 | 8.15 | 1.3 |
| 21 | 3TB3PenOH | 2.0 | −40 | >99 | 39 | 61 | 5.97 | 1.6 |
| 22 | neoPenOH | 2.0 | −40 | >99 | 27 | 73 | 2.78 | 1.5 |
| 23 | TMSiMeOH | 2.0 | −40 | 86 | 27 | 73 | 2.30 | 1.5 |
| 24 | 33DMeBuOH | 2.0 | −40 | >99 | 32 | 68 | 4.50 | 1.6 |
| 25 | TMSiEtOH | 2.0 | −40 | 88 | 32 | 68 | 3.56 | 1.6 |

a. [NIPAAm]$_0$ = 0.5 mol L$^{-1}$, [$n$-Bu$_3$B]$_0$ = 0.05 mol L$^{-1}$.

b. Determined by $^1$H NMR (methylene signals).

c. Determined by SEC (polystyrene standards).

d. Polymerization time = 2 h.

e. Monomer, polymer or both were precipitated during the polymerization reaction.

f. Data taken from Ref. 12.