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A Novel Synthetic Method of Polymeric Alcohols. Step-Polymerization of Diketones with Distyryl Derivatives Promoted by Samarium Iodide

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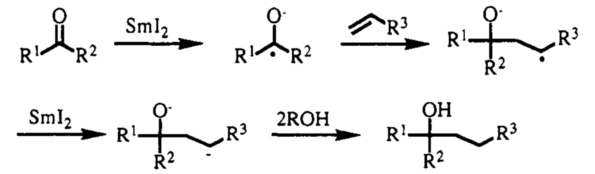
Electron-transfer reaction has been established as a powerful methodology in the field of organic synthesis.[1] The most characteristic point of electron-transfer reaction is that it can easily generate various active species such as a cation radical, an anion radical, anion, cation, and so on. Some polymerization methods utilizing electron-transfer reaction as a key step have been reported, for instance, electrolytic polymerization of aromatic compounds,[2] low-valent titanium-induced polymerization of carbonyls affording poly(pinacol)s or poly(phenylenevinylene)s,[3] and reductive coupling of silyl dihalides by alkaline metal to form polysilanes.[4]

In recent years, much attention has been paid to lanthanide elements based on their particular and characteristic reactivities. Among them, divalent samarium reagents, such as SmI_2 and $SmCp_2$, have been known as versatile one-electron reducing agents (−1.55 V vs SCE), and many unique reactions induced by Sm(II) as reaction initiators or coreagents have been described.[5] As an example of the characteristic reactions promoted by SmI_2, reductive cross-coupling of ketones with various olefins has been reported[6] (Scheme 1).

This reaction is initiated by electron transfer from SmI_2 to ketones forming ketyl radicals. The radicals attack double bonds to afford anion-radical species which are further reduced by SmI_2 and protonated by a coexisting alcohol. Although this coupling reaction can be accomplished by metal, photolysis, and electrolysis reductions,[1-7] these methods can be applied to only intramolecular cyclization in almost all cases. On the other hand, cross-coupling reactions of ketones with various olefins by use of SmI_2 proceed in excellent yields under mild conditions.[6] The application of these reactions to bifunctional compounds, for instance, diketones and diolefins, would offer the possibility to afford poly(alcohol)s having various functional groups in the main chain.[8] Poly(alcohol)s will be expected to be significant material, such as coatings, adhesives, and polymeric reagents.[9] In this paper, we describe step-polymerization of diketones with distyryl compounds using SmI_2 as an electron-transfer agent (Scheme 2).

As 4-equiv of SmI_2 and a proton source of diketone (stoichiometric amount) are fundamentally essential for the reaction, a slight excess of SmI_2 (ca. 4.5 equiv to diketone) was employed. Polymerization of *p*-bis(3-oxobutyl)benzene (**1a**) with *p*-divinylbenzene (**2a**) was examined to optimize the reaction conditions. The polymerization was carried out at room temperature in the presence of HMPA and *tert*-butyl alcohol using a 0.1 M SmI_2 solution in THF. After consumption of monomers (ca. 5 min), THF was removed, and the reaction mixture was poured into ether. The ether-insoluble part was extracted with THF and purified by reprecipitation into 3% HCl. The results are shown in Table 1.

Scheme 1



Scheme 2

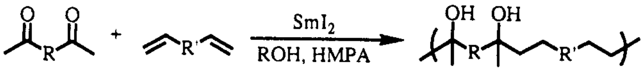


Table 1. Polyaddition of 1a to 2a under Some Conditions[a]

run	*t*-BuOH (equiv)	HMPA (mL)	yield (%)[b]	$\bar{M}_n$[b,c]
1	4	2	36	7500
2	8	2	49	11600
3	20	2	60	9000
4	30	2	60	7300
5	20	1	81	4000
6	20	0.5	56	2200

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), rt, SmI_2 (4.5 equiv). [b] Ether-insoluble part. [c] Estimated by GPC (THF, PSt standards).

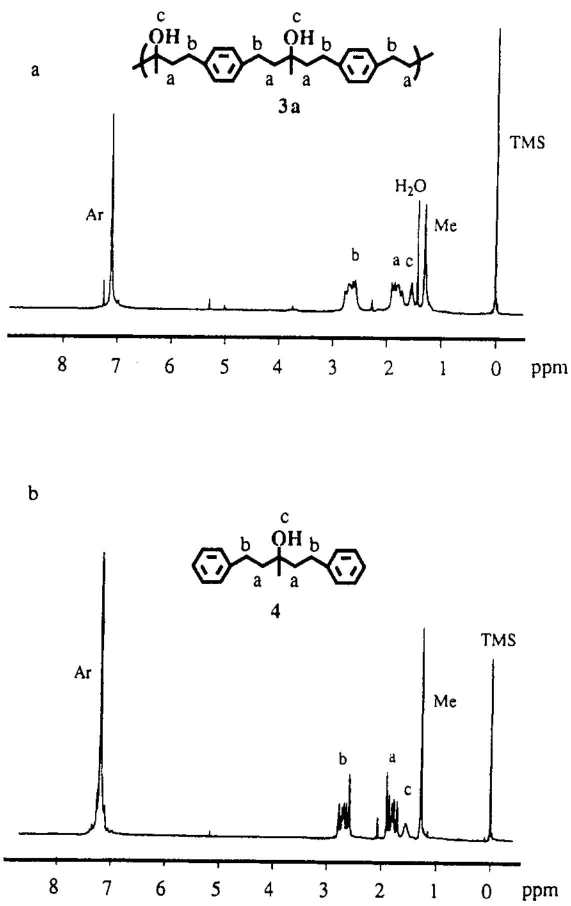


Figure 1. ^{1}H-NMR spectra of **3a** and **4a**.

In runs 1–4, the effect of the quantity of *tert*-butyl alcohol to **1a** on the molecular weight of the polymer was examined. In all cases corresponding polymers ($\bar{M}_n$ > 7300) were obtained, and it was found that the yields of the ether-insoluble parts decreased with decreasing of the amount of *tert*-butyl alcohol. HMPA was indispensable in the polymerization, and the quantity of HMPA affected the molecular weights of the polymer. The results of runs 3, 5, and 6 indicate that more than 2 mL of HMPA per 1 mmol of carbonyl group was essential to form high molecular weight polymer. From these results, the polymerization using 2 mL of HMPA and 20 equiv of *tert*-butyl alcohol to the carbonyl group might be the best

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Table 2. Dependence of $\bar{M}_n$ on the Feed Ratio of 1a to 2a

run	1a (mmol)	2a (mmol)	2a/1a	$\bar{M}_n{}^{a,b}$
1	0.488	0.262	0.54	3700
2	0.503	0.367	0.73	5000
3	0.489	0.488	1.00	9000
4	0.477	0.533	1.16	2200
5	0.500	0.717	1.43	550

[a] Ether-insoluble part. [b] Estimated by GPC (PSt standards).

conditions. The resulting polymer (**3a**) was soluble in common organic solvents such as THF, methanol, dichloromethane, and chloroform.

^{1}H-NMR and ^{13}C-NMR spectra of **3a** and the corresponding model compound (**4**), prepared by reductive coupling of benzylacetone with styrene, are shown in Figures 1 and 2, respectively.

All of the proton signals of **3a**, 7.10 (aromatic), 2.48–2.95 and 1.60–1.95 (methylene), and 1.28 ppm (methyl), are in good agreement with the model compound **4** (Figure 1a,b). Similarly, all of the carbon signals could also be assigned and agreed well with **4** (Figure 2a,b). In addition, the IR spectrum of the obtained polymer showed characteristic absorption due to O–H stretching. From these results it can be concluded that **3a** has the proposed structure bearing a tertiary alcohol unit in the main chain.

The stoichiometry of the employed two monomers is significant in the step-polymerization. Therefore, the effect of the feed ratio of the monomers on the molecular weight of the polymer was examined in the polymerization of **1a** with **2a** (Table 2).

As shown in Table 2, when the feed ratio of **1a** to **2a** approached unity, the molecular weight of the polymer increased as is usual for step-polymerization. Considering that the ketyl radical formed by one-electron reduction of ketone acts as the active species, these results indicate that conversion of ketone to the ketyl radical proceeds quantitatively, and the ketyl radical reacts with double bonds selectively. In other words, pinacol coupling, the most probable side reaction, scarcely occurred in this polymerization. It was also supported by the result that no peak was observed around 60 ppm in the ^{13}C-NMR spectrum except for the quaternary carbon attached to the hydroxyl group.

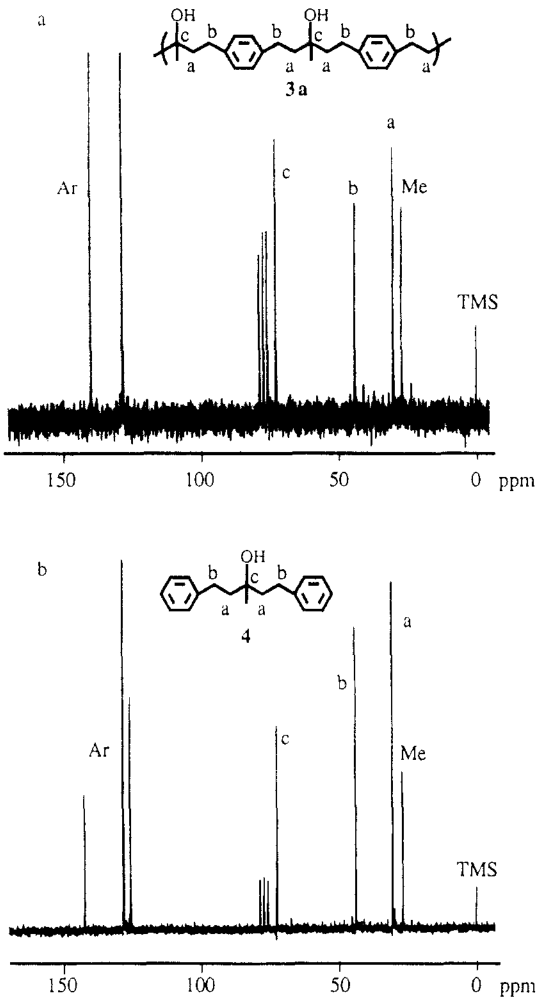
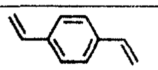
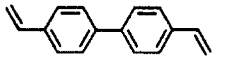
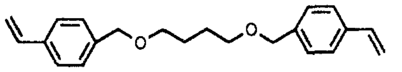
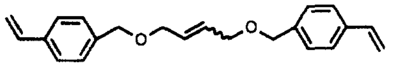
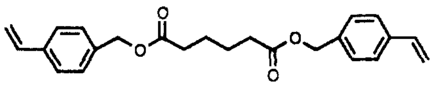
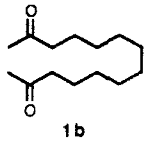


Figure 2. ^{13}C-NMR spectra of **3a** and **4a**.

The molecular weights of the obtained polymers were relatively low and the ether-soluble part contained lower molecular weight oligomers ($\bar{M}_n$ < 700), which indicates the existence of termination reactions. In the ^{1}H-NMR spectrum of the ether-soluble part, the signals attributed to the styryl group (5.1–6.9 ppm) and the secondary alcohol unit (3.8 ppm) could be observed. The possible termination reaction would be simple reduction of the carbonyl group resulting from hydrogen abstraction of the ketyl radical and/or further reduction of the ketyl radical to the

Table 3. Polyaddition of Diketones with Distyryl Compounds

diketone	distyryl compd		yield (%)	$\bar{M}_n$ $(\bar{M}_w/\bar{M}_n)^b$
1a		**2a**	60	9000 (1.4)
		**2b**	46	2800 (1.2)
		**2c**	66	6400 (1.2)
		**2d**	65	4600 (1.5)
		**2e**	55	6000 (1.3)
 1b		**2a**	41	6000 (1.2)

[a] Ether-insoluble part. [b] Estimated by GPC (THF, PSt standards).

corresponding anion.

The present step-polymerization could be applied to various distyryl compounds (**2b**–**e**). The results are summarized in Table 3. 4,4′-Divinylbiphenyl (**2b**) and ether-containing monomer **2c** gave corresponding polymers in moderate yields. Interestingly, the polymerization of **1a** with **2d**, which has an internal double bond, proceeded without attack of the ketyl radical on the internal double bonds. Furthermore, polymerization of **1a** with **2e** bearing an ester moiety afforded a corresponding polymer which has both tertiary alcohol and ester groups in the main chain. In this case, the ester groups were neither hydrolyzed nor reduced by SmI_2 during polymerization. Linear diketone, 2,13-dioxotetradecane (**1b**), was also available as a monomer to produce polymer **3f** by reaction with **2a**.

In summary, novel multifunctional polymers having tertiary alcohols together with various functional groups in the main chain could be provided by utilizing reduction coupling of ketones with olefins. This polymerization method *via* an electron-transfer process would propose a new synthetic method for multifunctional poly(alcohol)s from the corresponding ketones with unsaturated compounds.

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