Polyaddition of Diketones with Bis(phenylacetylene) Derivatives *via* Electron Transfer. Preparation of Polymers Containing an Allyl Alcohol Moiety in the Main Chain

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Polymers containing hydroxyl groups are one group of significant and characteristic materials that can be applied to coatings, adhesives, polymeric reagents, and so on.[1] In spite of their useful application, general synthetic methods for the preparation of the polymers having hydroxy groups attached to the main chain are quite limited so far. Previously, we have reported a new synthetic method for the preparation of polymers having hydroxy groups at the main chain by polyaddition of diketones to distyryl compounds utilizing samarium(II) iodide as an electron-transfer agent.[2] In this polyaddition, distyryl compounds having various functional groups such as ether, ester, and double bond groups are also available as monomers which give corresponding polymers without serious side reaction (Scheme 1).

This reaction proceeds *via* electron transfer from Sm(II)[4] to ketones to generate ketyl radicals that can attack the double bonds. The resulting radical may be further reduced to anionic species affording the corresponding alcohol by the protonation of it.[4] Further, this reaction has been applied to acetylene derivatives to give allylic alcohols.[5] In this paper, we describe polyaddition of diketones with bis(phenylacetylene) derivatives using SmI_2 as an electron-transfer agent (Scheme 2).

As a model reaction, reductive coupling of benzylacetone with phenylacetylene was examined to optimize the reaction conditions for the polyaddition (Scheme 3). The reaction was carried out using benzylacetone (0.5 mmol) and phenylacetylene (0.5 mmol) in the presence of alcohols (2 equiv to the carbonyl group) and various amounts of HMPA (1.5–9 equiv to SmI_2) using 12 mL of a 0.1 M SmI_2 solution in THF. The results are summarized in Table 1. As a proton source, *tert*-butyl alcohol gave better results compared with methanol and isopropyl alcohol. The yield decreased as the reaction was carried out at 0 °C because the rate of attack of the ketyl radical to the triple bond might decrease. On the other hand, a high temperature (40 °C) resulted in decreasing the yield of **4**, probably due to side reactions such as aldol condensation. The addition of HMPA was necessary to the reductive coupling and affected the yields of the product. It was found that the yield of the coupled product showed the highest value when 9 equiv of HMPA to SmI_2 was employed. The obtained coupled products contain two isomers (*E* and *Z* forms), and the ratios of *E* and *Z* isomers did not depend on these reaction conditions. From these results, the conditions of run 3 would be suitable for the desired polyaddition.

The polyaddition was carried out under suitable conditions obtained from the model reaction by use of *p*-bis(3-oxobutyl)benzene (**1a**) that was prepared by the condensation of ethyl acetoacetate with *p*-xylylene dibromide followed by decarboxylation with *p*-diethynylbenzene (**2a**) as monomers (Scheme 4). After consumption of the monomers, the reaction mixture was reprecipitated with ether. The ether-insoluble part was dissolved into THF, and the solution was reprecipitated with water several times to remove the inorganic compounds. The results of the polymerization are shown in Table 2.

The yields of the polymers and their number-average molecular weights increased as the feed ratio of **1a** to **2a**

Table 1. Cross Coupling of Benzylacetone with Phenylacetylene[a]

run	ROH	HMPA (equiv)[b]	temp (°C)	yield (%)[c]	*E*/*Z*[d]
1	MeOH	9	rt	67	79/21
2	*i*-PrOH	9	rt	59	84/16
3	*t*-BuOH	9	rt	81	89/11
4	*t*-BuOH	9	40	76	83/17
5	*t*-BuOH	9	0	67	87/13
6	*t*-BuOH	6	rt	73	75/25
7	*t*-BuOH	3	rt	72	71/29
8	*t*-BuOH	1.5	rt	63	80/20

[a] Reaction conditions: benzylacetone (0.5 mmol), phenylacetylene (0.5 mmol), rt, SmI_2 (1.2 mmol), ROH (1.0 mmol). [b] Equiv to the carbonyl group. [c] Isolated yields. [d] Determined by ^1H NMR.

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]	$\bar{M}_w/\bar{M}_n$[a,b]
1	0.454	0.322	0.71	2700	1.6
2	0.451	0.399	0.89	3200	1.9
3	0.517	0.515	1.00	4200	1.5
4	0.497	0.566	1.13	2400	2.0
5	0.453	0.519	1.31	1800	1.6

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

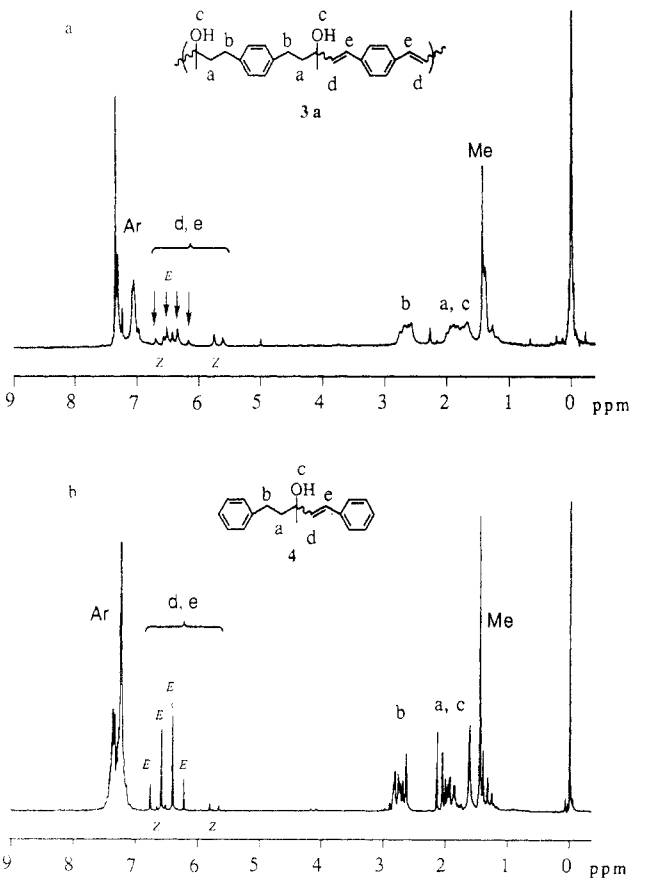

Figure 1. ^1H-NMR spectra of **3a** and **4**.

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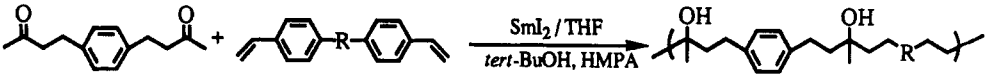
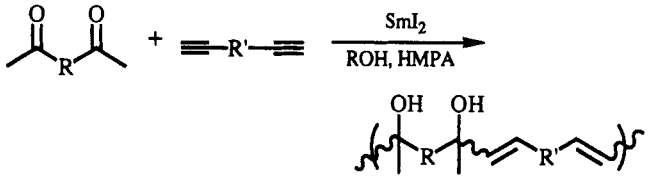
Scheme 1

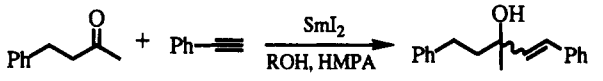


Distyryl Compounds ; *p*-Divinylbenzene ($\bar{M}_n$=9000)
R = nil ($\bar{M}_n$=2800)
R = $CH_2O(CH_2)_4OCH_2$ ($\bar{M}_n$=6400)
R = $CH_2OCH_2CH{=}CHCH_2OCH_2$ ($\bar{M}_n$=4600)
R = $CH_2O_2C(CH_2)_4CO_2CH_2$ ($\bar{M}_n$=6300)

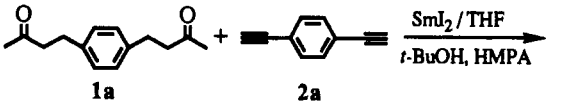
Scheme 2



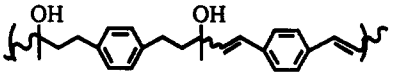
Scheme 3



Scheme 4



1a **2a**



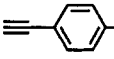
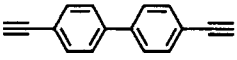
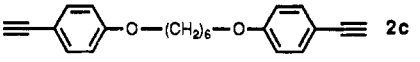
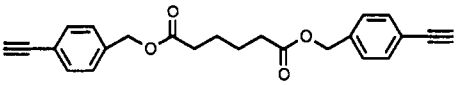
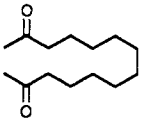
3a

approached to 1:1, indicating that the polyaddition proceeds without serious side reactions. In other words, attack of the ketyl radical on the styryl unit in the main chain and pinacol coupling might be negligible. The obtained polymer **3a** was soluble in common organic solvents such as chloroform, methanol, and DMF. The IR spectrum of the polymer showed the characteristic absorption of the OH group at 3100–3360 cm^{-1} together with ones at 1604, 972, and 738 cm^{-1} attributable to the C–C double bond. The ^1H NMR spectra of **3a** and the model compounds **4** measured in $CDCl_3$ are shown in parts a and b of Figure 1, respectively. All of the proton signals of **3a** could be assigned as illustrated in Figure 1a and agreed well with the model compound **4**. The ratio of signal intensities of olefinic (5.5–6.8 ppm) and methylene protons attached to the aromatic ring (2.5–2.8 ppm) was almost 1:1. These spectral data may support strongly that the resulting polymer consists of one unit formed by selective addition of the ketyl radical to the terminal triple bond of **3a**.

Polyaddition of diketones with bis(phenylacetylene) derivatives having various functional groups was also examined (Table 3). Similar to **2a**, 4,4′-diethynylbiphenyl (**2b**) and oxygen-containing monomer (**2c**) also give corresponding polymers in good yields. The polymer having both an allylic alcohol unit and an ester moiety was cleanly obtained from **2d** without reduction or hydrolysis of the ester group. The molecular weights of the resulting polymers were relatively lower than those from distyryl compounds because of lower reactivity of the triple bond than that of the double bond. Linear diketone (**1b**) was also available as a monomer in the present polyaddition affording corresponding polymers (runs 5 and 6). In all cases, the resulting polymers were soluble in common organic solvents. Newly formed carbon–carbon double bonds in the polymers contained both *E* and *Z* forms. Assignment of the stereochemistry has been made by comparison with the ^1H-NMR spectrum of the model compound (Figure 1). The ratios of the *E* and *Z* structures were estimated by ^1H NMR using the ratio of signal areas for olefinic protons. As illustrated in Table 2, *E* structures were major products in all cases, and increasing the electron density of the triple bond tends to increase the ratio of the *E* form.

In conclusion, the present work could demonstrate that a ketyl radical derived from a ketone by electron-transfer reaction could be utilized for selective radical polyaddition

Table 3. Polyaddition of Diketones with Various Bisphenylacetylene Derivatives

diketones	bisphenylacetylene derivatives	yield (%)[a]	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[a,b]	*E*/*Z*[c]
1a	 **2a**	64	4200 (1.5)	54/46
	 **2b**	82	2000 (1.9)	65/35
	 **2c**	75	3500 (2.0)	90/10
	 **2d**	48	2200 (1.4)	88/12
 **1b**	**2a**	44	3200 (1.3)	53/47
	2c	63	4400 (1.7)	70/30

[a] Ether-insoluble part. [b] Estimated by GPC (THF, polystyrene standards). [c] Determined by ^1H NMR.

to a triple bond, affording polymers containing an allyl alcohol moiety in the main chain. Further work on the polyadditions of diketones to other unsaturated compounds as well as applications of the resulting polymers to functional materials is in progress.

References and Notes

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(4) The radical mechanism has been supported by the result of cross coupling of styrene with 4-*tert*-butylcyclohexanone.[5]
(5) Inanaga, J.; Katsuki, J.; Ujikawa, O.; Yamaguchi, M. *Tetrahedron Lett.* **1991**, *32*, 4921.