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Novel Solid-State Polymerization of Crystalline Monomer. Dehydrative Polycondensation of 1,3-Bis(hydroxyphenylmethyl)benzene

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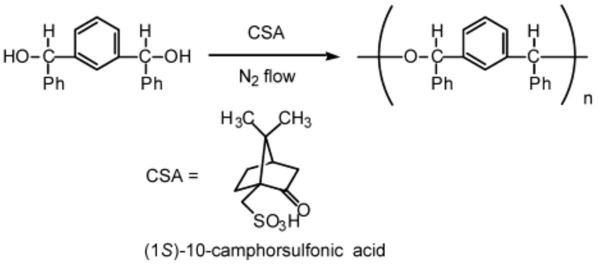
Organic reactions are usually carried out in a liquid phase. However, pioneering works of Toda et al. have demonstrated that a number of reactions proceed even in the solid state.[1] Rothenberg et al. have recently reported that some of them virtually take place in the liquid state,[2] while it is also true that unique selectivity or reactivity has been found in many solvent-free reactions, some of which have proved to proceed in the solid state.[1] In the field of polymerization chemistry, "solid-state polymerization" has been actively studied in the 1960s.[3] Although some recent works are opening new aspects,[4,5] further study increasing the variety is necessary to disclose the potential of solid-state polymerization.

Thus, we have undertaken a project of developing novel solid-state polymerizations, beginning it by extending known solid-state organic synthesis to the reaction of a bifunctional compound. In this context, very recently, the solvent-free oxidative coupling polymerization of 2,6-dihydroxynaphthalene with $FeCl_3 \cdot 6H_2O$ has been found in our laboratory.[6] Herein, our attention was given to solid-state self-condensation of diphenylmethanol which produces the ether by the treatment with *p*-TsOH.[7] We designed 1,3-bis(hydroxyphenylmethyl)benzene (**1**) as the bifunctional compound for polycondensation and succeeded in isolating one of two diastereomers of **1**, i.e., the racemic modification (*rac*-**1**). Although another diastereomer, the meso form, has not been isolated yet, the very interesting finding prompted us to publish this communication urgently: The polycondensation of *rac*-**1** successfully takes place in the solid state and gives the polyether having an unexpectedly high molecular weight.

In the original procedure reported by Toda et al., an equimolar amount of p-TsOH$\cdot H_2O$ was ground with the crystal of diphenylmethanol.[7] Herein, we use (1*S*)-10-camphorsulfonic acid (CSA), which is less hygroscopic and has the higher melting point of 196−200 °C, in place of p-TsOH$\cdot H_2O$ (mp 103−106 °C).

As the first attempt, *rac*-**1** (mp 158−160 °C) was ground with 200 mol % of CSA, which is the equimolar amount for the hydroxy groups, and the mixture was gradually heated under air in order to optimize the reaction temperature. Consequently, *rac*-**1** was found to be almost quantitatively polymerized at 100 °C for 6 h to produce the expected polyether (M_p (molecular weight at the peak top of a GPC profile) = 14 500). It should be noted that the reaction mixture was a white powder throughout the polymerization. Theoretically, CSA is the catalyst to activate the hydroxy group, so that the polymerization using a catalytic amount of CSA was investigated. The well-ground mixture of *rac*-**1** with 5 mol % of CSA was heated under a nitrogen flow as illustrated in Figure 1. Very interestingly, the high molecular weight polymer was found to be produced in the solid state by the catalytic reaction (Table 1). Three reaction batches were carried out, tracing the polymerization process (runs 1−3, 4−7, and 8−11). It should be emphasized again that the reaction mixtures showed no change in appearance, being white powder, during these runs.



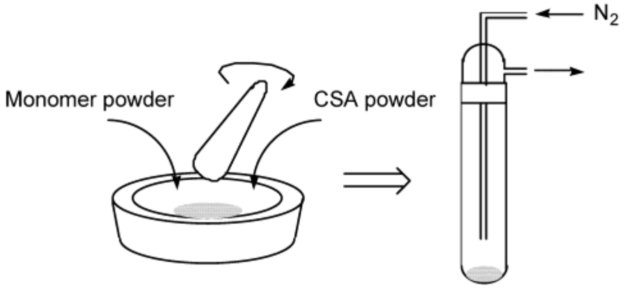


Figure 1. Solid-state dehydrative polycondensation.

The monomer conversion increased with reaction time, finally reaching 90−100%, and was remarkably promoted by raising the temperature a little (10 °C). It is noteworthy that the high molecular weight polymer is produced even at the early stage of the polymerization. This finding is contrary to the theory of step polymerization: Oligomer should be exclusively produced before the complete conversion of monomer. Thus, the reaction mixtures were analyzed by using powder X-ray diffraction (Figure 2). There are observed peaks due to the crystalline monomer along with a broad halo peak due to the noncrystalline polymer produced. This observation means that the polymerization takes place locally: Once the polymerization starts at defects of the monomer crystal, the polymer is rapidly produced therein. The catalyst proton is probably carried around with a trace amount of water generated.

It is also unusual that the molecular weight of the product polymer does not increase with increasing monomer conversion. At 100 °C, the molecular weight was almost constant during the reaction period of 24 h and then gradually decreased with time (runs 1−7). In the reaction at 110 °C, it reached the maximum after 5 h, which was followed by the rapid decrease. These findings indicate that cleavage of the polymer main chain is also involved under the polymerization conditions. Thus, the isolated polyether (M_w = 46 800, M_n = 27 600) was ground with 50 mol % of CSA and heated at 100 °C under a nitrogen flow. As shown by GPC

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Table 1. Solid-State Polymerization of *rac*-1 with 5 mol % of CSA

run	temp (°C)	time (h)	conv[a] (%)	M_p[b]	M_n[b]	M_w[b]	M_w/M_n[b]
1	100	5	30	30 000	17 900	32 300	1.8
2	100	11	43	31 000	16 200	32 100	2.0
3	100	24	58	33 000	17 500	34 600	2.0
4	100	24	59 (57)	39 300	18 600	36 700	2.0
5	100	48	76 (72)	31 700	16 600	33 500	2.0
6	100	72	77 (80)	22 000	10 000	26 100	2.6
7	100	120	90 (83)	13 300	*c*	*c*	*c*
8	110	1	36	31 000	14 100	31 400	2.2
9	110	5	89	53 200	21 300	43 100	2.0
10	110	11	100	34 500	16 200	35 400	2.2
11	110	24	97	26 600	14 900	32 400	2.2

[a] Monomer conversions were calculated by GPC profiles of the reaction mixtures. In runs 4−7, the conversions evaluated by ^{1}H NMR spectra are also shown in the parentheses. See Supporting Information for details about the calculation. [b] M_p values represent molecular weights at the peak tops of GPC profiles (eluent: $CHCl_3$, calibrated with polystyrene standards). Other values are also evaluated from GPC profiles. [c] Insufficient peak separation between *rac*-1 and the polymer did not allow the calculation.

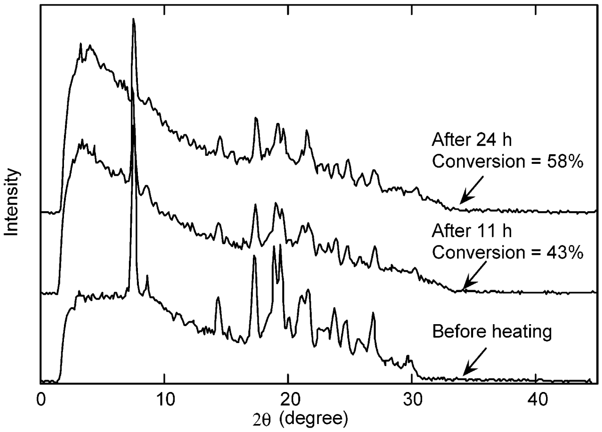

Figure 2. Powder X-ray (Cu Kα radiation, $\lambda = 1.5418$ Å) diffraction patterns of *rac*-**1** heated with CSA (5 mol %) at 100 °C.

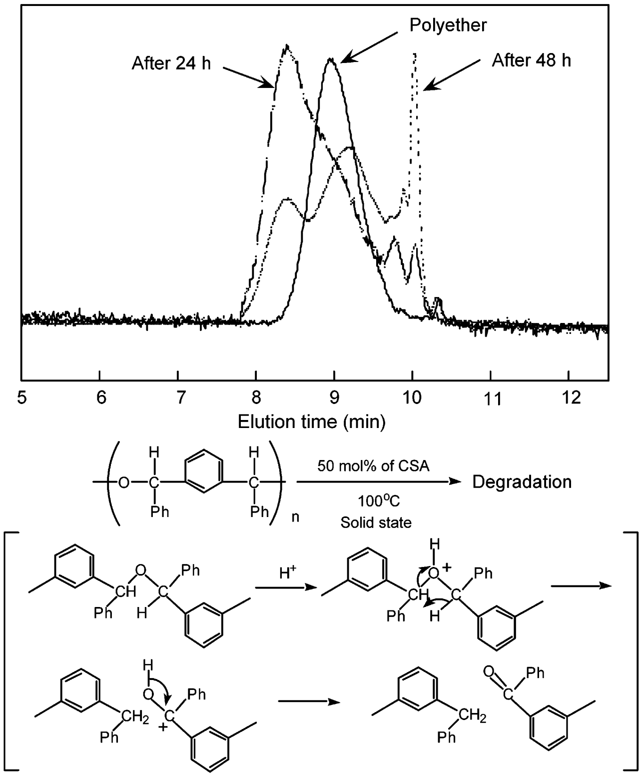

Figure 3. GPC profiles in the degradation experiment of the polyether (upper) and the degradation mechanism (lower).

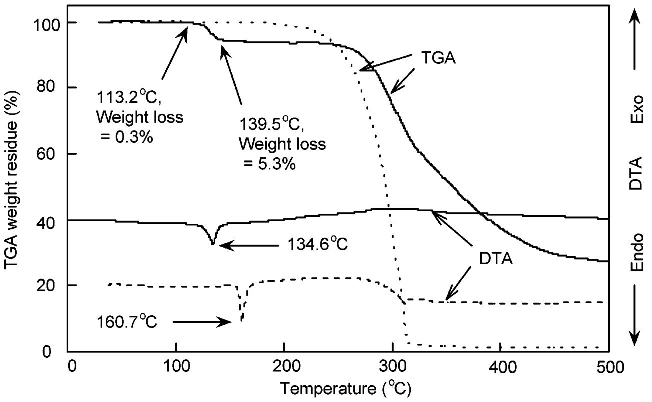

Figure 4. TG-DTA profiles of *rac*-**1** with (solid lines) and without (dashed lines) 5 mol % of CSA (heating rate = 10 °C/min).

analyses in Figure 3, the heating for 24 h increased the molecular weight of the polyether in the solid state, but degradation of the polymer chain was apparently included after 48 h. IR and ^{1}H NMR analyses of the reaction mixture suggested the formation of benzophenone and diphenylmethane moieties, showing an IR peak at 1660 cm^{-1} ($\upsilon_{C=O}$), multiple NMR signals around δ 7.6 ppm (aromatic protons with an electron-withdrawing substituent), and a singlet NMR signal at δ 3.87 ppm (methylene protons between two aromatic rings). The plausible degradation mechanism is shown in Figure 3. A similar reaction of bis(diphenylmethyl) ether has been proposed in a previous work.[8]

Thermogravimetric and differential thermal analyses (TG-DTA) gave more information about this solid-state polycondensation. The ground powder samples of *rac*-**1** with and without CSA (5 mol %) were heated at a rate of 10 °C/min under a nitrogen flow (Figure 4). The DTA curve of the sample not containing CSA shows an endothermic peak corresponding to the melting point at 160.7 °C. On the other hand, in DTA of the sample containing CSA, an endothermic peak observed at 134.6 °C is ascribable to vaporization of water generated by the polycondensation, which is supported by TGA; a weight loss of 5.0%, which is consistent with the theoretical value of 6.0% due to the polycondensation, is observed between 113.2 and 139.5 °C. It is also noteworthy that the degradation curves of the two samples in TGA are much different. Without CSA, the sample rapidly decomposes and almost completely volatilizes out around 300 °C. In the presence of CSA, the sample gradually decomposes and gives the residue of 27 wt % even at 500 °C. These findings also imply the polymer formation with the aid of CSA.

Finally, we touch on the ^{1}H NMR spectrum of the polyether produced. There are observed very closely splitting signals (δ 5.21, 5.22, and 5.24 ppm) for the methine protons, which is probably due to the tacticity. Further study is under way.

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Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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