Thermally Induced Topochemical Polymerization of 1,3-Diene Monomers

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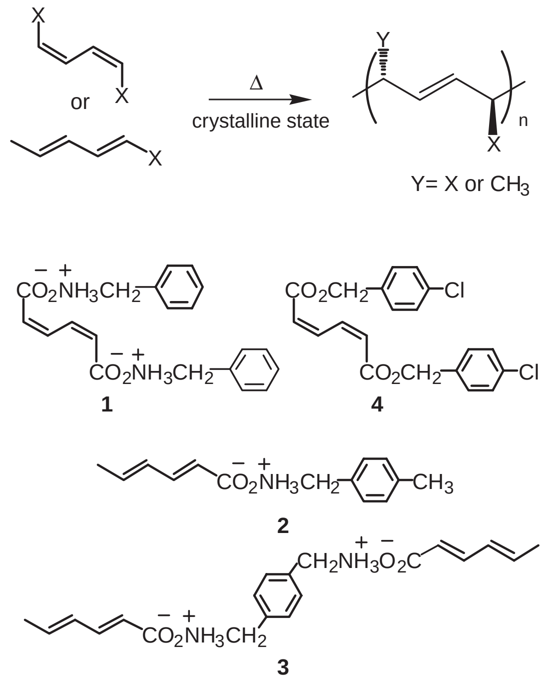
The topochemical polymerization of the 1,3-diene compounds such as the ammonium and ester derivatives of the muconic and sorbic acids is induced by heating without any irradiation in the crystalline state.

Recent developments in crystal engineering and supramolecular chemistry include the potential that topochemical polymerization will be one of general methods for polymer production in the future, similar to polymerization in the gaseous or liquid state. Some unsaturated compounds such as the diolefin,[1] 1,3-diene,[2–6] diacetylene,[7] and triacetylene[8] derivatives are topochemically polymerized in the crystalline state under UV, X-, and γ-ray irradiation. Acetylene derivatives also provide a polymer upon heating of the crystals. Thermally induced polymerization is more excellent than UV- or γ-ray irradiation polymerization from the viewpoint of handling, reproducibility, and safety. In many photoreaction cases in the solid state, the quantitative and kinetic analysis of the photoreaction is disturbed by heterogeneous irradiation conditions, because the incident light is absorbed around the surface of the solid.

We have already reported that the 1,3-diene monomers are polymerized by UV, X-, and γ-ray irradiation in the crystalline state. However, no thermally induced polymerization has ever been detected, because typical polymerizable monomers such as diethyl (*Z*,*Z*)-muconate,[2] benzylammonium (*Z*,*Z*)-muconate (**1**),[9] and 4-methylbenzylammonium sorbate (**2**)[10] melt or decompose upon heating; the melting point is 53 °C for diethyl (*Z*,*Z*)-muconate, and **1** and **2** decompose over 100 °C. Recently, we determined the thermally induced topochemical polymerization of *p*-xylylenediammonium disorbate (**3**)[11] and 4-chlorobenzyl (*Z*,*Z*)-muconate (**4**)[12] (Scheme 1), which have high decomposition and melting points of over 160 °C and 131 °C, respectively.

The monomer crystals of **1–4** were heated at 80–120 °C for 6 h in the dark under atmospheric conditions (Table 1). Monomers **1** and **2** partly decomposed during polymerization over 100 °C, resulting in a low polymer yield. In contrast, the polymer yield of **3** and **4** increased as the reaction temperature increased, and reached a 96% yield at 110 °C for **4**.

Polymers from the thermally induced polymerization of the monomers **1–4** were insoluble in all solvents including the common solvents, similar to the photopolymers. The obtained polymers **1–3** were characterized by ^{13}C NMR after transformation of the countercations. It has been previously reported that the alkylammonium muconate or sorbate derivatives are transformed into a polymer soluble in water or methanol through polymer reactions.[9–11,13] We have confirmed that the polymers obtained from the thermally induced polymerization have a structure identical to a stereoregular *meso-* or *erythro*-diisotactic-*trans*-2,5-polymer produced by UV- or γ-ray irradiation. The powder X-ray diffraction pattern of poly(**3**) consists of sharp reflections, similar to that of the polymer obtained by photo-irradiation. These results indicate that the crystalline state is maintained during the thermally induced polymerization of **3**, and that the thermally induced polymerization proceeded without any molecular disorder in the crystalline state, being different from the polymer derived from lithium sorbate as reported in the literature.[6]



Scheme 1.

Table 1. Thermally Induced Topochemical Polymerization of 1,3-Diene Monomers in the Dark for 6 h under Atmospheric Conditions

Temp /°C	Polymer Yield/%			
	1	**2**	**3**	**4**
80	4	5	1	27
90	9	14	5	36
100	17[a]	21[a]	10	78
110	22[a]	6[a]	30	96
120	15[a]	1[a]	66	—

[a] Partly decomposed during polymerization.

Figure 1 shows the relationship between the polymer yield and time, and their first order plots during the thermally induced polymerization of **3** at 100 °C in the dark and under UV irradiation using a high-pressure lamp at a distance of 30 cm. The rate

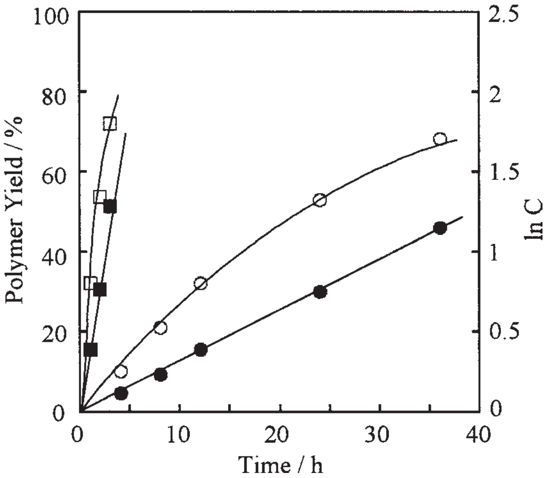


Figure 1. Relationship between the time and the polymer yield during the thermally induced polymerization of **3** at 100 °C; in the dark (○), under UV irradiation (□) using a high-pressure Hg lamp at a distance of 30 cm. Closed symbols indicate the first order plot for the polymerization in the dark (●) and under UV irradiation (■).

constant (k) of the thermally induced polymerization at 100 °C in the dark and with UV irradiation are $8.8 \times 10^{-6}\,\mathrm{s}^{-1}$ and $1.1 \times 10^{-4}\,\mathrm{s}^{-1}$, respectively. The reaction rate of the thermally induced polymerization by UV irradiation is over 10 times faster than in the dark. On the other hand, the polymer yield of the photoirradiation at room temperature for 24 h at the distance of 10 cm is low (28%). The reaction rate of the photo-polymerization at room temperature is low as that of the thermally induced polymerization. Namely, the thermally induced topochemical polymerization by UV irradiation is effective for a quantitative polymer yield within a short time.

During both the thermally and photo-induced polymerization, a heterogeneous reaction is involved as the propagation process,[14] but the initiation steps are different from each other. During the photo-induced polymerization, a unimolecular initiation is caused by the excitation of diene part and a bimolecular initiation is also possibly included owing to the crystal-lattice strain. In contrast, the thermally induced polymerization contains only a bimolecular initiation as the initiation step for producing free radicals. The difference in the reaction mechanisms between the thermally and photo-induced polymerizations will be investigated in future work. It will help us to fully understand the mechanism of the topochemical polymerization in the solid state.

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