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(11) The polymer was modeled by 1,5-dimethyl-1,1,2,2,3,3,4,4,5,5-deca-*n*-hexylpentasilapentane.[7]

(12) For C_{sp^3}, $R^* = 1.950$ Å and EPS = 0.044.

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Monomer-Isomerization Radical Polymerization of Di-*tert*-butyl Maleate to High Molecular Weight Poly(di-*tert*-butyl fumarate)

We have found that di-*tert*-butyl fumarate (**1**) is obtained quantitatively through isomerization of di-*tert*-butyl maleate (**2**) in the presence of a catalytic amount of morpholine. Moreover, when the reactions of isobutene with fumaric acid and maleic acid were carried out in the presence of sulfuric acid catalyst in diethyl ether to prepare **1** and **2**, respectively, the yield of **2** was higher than that of **1**, because of high solubility of maleic acid in ether. As described in a previous paper,[1] **1** was polymerized quite easily with a radical initiator to give a high molecular weight nonflexible rodlike poly(di-*tert*-butyl fumarate), poly(*tert*-butoxycarbonylmethylene) (**3**), which is then converted to poly(fumaric acid), poly(hydroxycarbonylmethylene) (**4**) on heating **3** at 180 °C (see Scheme I).

Scheme I

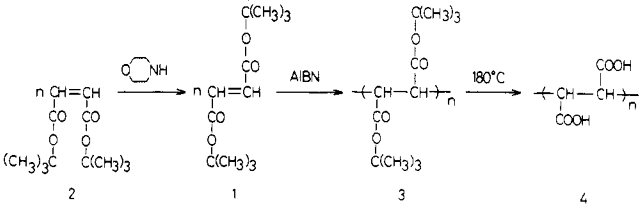

Table I
Results of Polymerization of 1 and 2[a]

compd	[morpholine], mol/L	yield, %	$\bar{M}_n \times 10^{-4}$ (GPC)
1	0	42	4.5
1	0.12	39	2.9
1	0.22	38	1.0
1	0.35	30	0.7
2	0	0	
2	0.08	17	1.1
2	0.16	25	1.0
2	0.22	27	0.9
2	0.27	25	0.8
2	0.35	23	0.7

[a] Polymerization conditions: [**1**] = [**2**] = 2.2 mol/L, [AIBN] = 2.2×10^{-2} mol/L in benzene; 60 °C; 10 h.

On the other hand, we have also found that dialkyl maleates do not homopolymerize with a radical initiator, 2,2′-azobis(isobutyronitrile) (AIBN), but they undergo homopolymerization with a monomer isomerization in the presence of AIBN and morpholine as an isomerization catalyst to yield high molecular weight polymers, which consist of similar structure to those obtained from the corresponding dialkyl fumarates; i.e., the maleates isomerize first to the fumarates, which then homopolymerize.[2-4] Similar monomer-isomerization polymerizations have been reported for various internal olefins with Ziegler-Natta catalyst.[5-7]

The most important merit of such monomer-isomerization polymerization in polymer synthesis is that compounds that have been known to be not homopolymerized are used as a new polymerizable monomer.[8] If **2** is polymerized via a monomer-isomerization radical polymerization mechanism, this reaction is a one-pot synthesis of **3**, from which **4** is easily derived.

The results of polymerization of **2** are shown in Table I, in which those of **1** are also indicated.

As reported previously,[1] **1** readily polymerizes with AIBN in the absence of morpholine, but **2** does not give any polymer. In the presence of both AIBN and morpholine, **2** undergoes polymerization, and the polymer yields increase with increasing morpholine concentration below ca. 2.0 mol/L and then decrease at higher concentrations. During polymerization, the isomerization of **2** to **1** was also observed, though its rate was slow compared with that of diethyl maleate to diethyl fumarate.[7] The addition of morpholine to radical polymerization of **1** decreased the yield and the molecular weight of the polymers. Therefore, morpholine seemed to act as both an isomerization catalyst of **2** to **1** and a retarder of radical polymerization of **1**.

When time-conversion relations for the monomer-isomerization radical polymerization of **2** with both AIBN and

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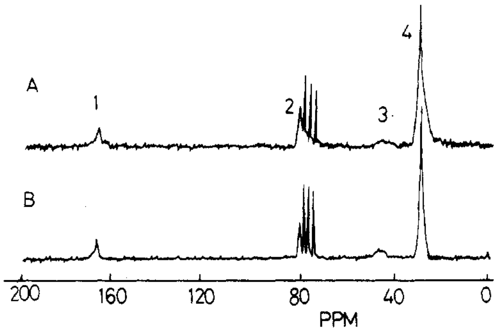

Figure 1. ^{13}C NMR spectra of polymers (A) from DtBF and (B) from the DtBF-morpholine system at room temperature in $CDCl_3$. Assignment: (1) carbonyl, (2) quaternary, (3) methine, and (4) methyl carbons.

morpholine were determined at 50, 60, and 70 °C, a short induction period was observed, and it shortened with increasing polymerization temperature, indicating that it corresponds to a time in which the concentration of **1** necessary to induce its homopolymerization is accumulated by the isomerization of **2**. Moreover, **2** was found to have almost no effect on the radical polymerization of **1**.

The ^{13}C NMR spectra of the polymers obtained from **1** and **2** are shown in Figure 1.

The spectra are essentially the same; i.e., the peaks at 28, 46, 81, and 170 ppm are due to methyl, methine, quaternary, and carbonyl carbons, respectively. Therefore, these results strongly suggest that the polymerization of **2** with both AIBN and morpholine proceeds via a monomer-isomerization radical polymerization mechanism; i.e., **2** isomerizes first to **1**, which then homopolymerizes to give **3**.

Polymer **3** obtained from **2** was also converted to poly(fumaric acid) (**4**) with quantitative elimination of isobutene when **3** was heated at 180 °C, the same as for **2** obtained from **1**.[1]

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