Cationic Ring-Opening Polymerization of 2-Isopropenyl-4-methylene-1,3-dioxolane at Ambient Temperature

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ABSTRACT: Monomer of an unsaturated cyclic acetal having two carbon-carbon double bonds, 2-isopropenyl-4-methylene-1,3-dioxolane (I) has been synthesized from methacrolein and epichlorohydrin using tert-butoxide as a catalyst, and polymerized via cationic mechanism at ambient temperature. Linear soluble polymer containing pendant isopropenyl group, II, was obtained from the cationic polymerization systems initiated by CH$_3$SO$_2$H at temperatures ranging from 0 to 60 °C in the presence of various nucleophilic additives or in the nucleophilic solvents. However, only crosslinked polymer, which is the product of simultaneous propagation of two carbon-carbon double bonds in I, was obtained without nucleophilic additive. This behavior was explained in terms of the stabilization of cationic species due to the interaction of cationic species with nucleophile.

**Introduction**

Selective polymerization of monomers having two similar polymerizable groups is generally difficult because both groups have a tendency to polymerize simultaneously.$^1$ In some cases, however, selective polymerization of such monomers without crosslinking has been achieved by cyclization polymerization$^6$ or polymerization under highly controlled conditions.$^{2,3}$ Highly functionalized and/or reactive polymers are usually prepared from the result of these polymerization techniques.

Recently, we reported cationic ring-opening polymerization of 2-isopropenyl-4-methylene-1,3-dioxolane (I), which has two cationically polymerizable carbon-carbon double bonds, enol ether and isobutene moieties.$^1$ A linear soluble polymer(poly(ketoether)) II, having isopropenyl pendant group from I was obtained from cationic polymerization of I by CH$_3$SO$_2$H initiation at -78 °C since polymerization proceeds by the preferential nucleophilic attack of enol ether part of monomer I to the cation IV which was quantitatively transformed from III (Eq. 1). Whereas only crosslinked polymer is obtained from the polymerization systems initiated by stronger acid such as BF$_3$OEt$_2$ or CF$_3$SO$_2$H at ambient temperature.

We have also found photo-initiated cationic polymerization of I using benzyl(4-hydroxyphenyl)methylsulfonium hexafluoroantimonate (BSS) as a photo-initiator at ambient temperature to produce poly(keto-ether) II without crosslinking.$^5$ We have proposed that a interaction between terminal cation and counter ligands, such as sulfides, released from BSS at the initiation step may stabilize terminal cation to depress crosslinking. As it has been reported in carbocationic living polymerization$^8$ in the presence of nucleophilic additive, it is believed that undesirable side reaction can be depressed by the addition of nucleophilic compound. In this case more nucleophilic enol ether moiety might selecti-
vely attack the terminal cation to form intermediate III, and subsequent ring-opening isomerization of III would occur quantitatively to afford terminal cation IV (Eq. 1). These results prompted us to examine cationic polymerization of I in the nucleophilic solvents or compounds at ambient temperature, especially by way of donor numbers (DN), which is one of parameter representing the nucleophilicity of the solvents. Herein, we wish to report the selective cationic ring-opening polymerization of I at ambient temperature in the presence of nucleophilic additive or solvent.

**Experimental**

**Measurements.** Gel permeation chromatography (GPC) measurement was carried out on a TOSOH HLC-8020 equipped with TSKgel G5000HXL, TSK-gel G4000HXL, and TSKgel G2500HXL columns eluted by tetrahydrofuran. The molecular weights of polymers were estimated from GPC calibrated with polystyrene standards. $^1$H and $^{13}$C NMR spectra were recorded on a JEOL PMX60Si or a JEOL EX-90 spectrometer. IR spectra were recorded on a JASCO FT/IR-3.

**Polymerization of I in the Presence of Nucleophilic Compounds.** To a solution of 0.50 g (4 mmol) of I prepared as previously reported and 0.08 mmol (2 mol%) of nucleophilic compounds in 8 mL of dichloromethane, was added 3.5 μL (1 mol%) of CF$_3$SO$_2$H under nitrogen atmosphere at ambient temperature, with stirring. After stirring for 30 min the reaction was stopped by addition of methanol containing NH$_3$ of equimolar amount to the catalyst, and the reaction mixture was evaporated to dryness under reduced pressure. Monomer conversion was evaluated by its residual weight after evaporation. The crude product was dissolved in dichloromethane (5 mL), and was poured into a large amount of hexane to precipitate the polymer. After the hexane layer was removed by decantation, the precipitate was dried under vacuum to obtain polymer. Structure of the obtained polymer was confirmed by IR and NMR spectra.

**Polymerization of I in Nucleophilic Solvents.** To a solution of 0.50 g (4 mmol) of I in 8 mL of dry solvents was added 2.5 mL (1 mol%) of CH$_3$SO$_2$H at ambient temperature in nitrogen atmosphere with stirring. The mixture was allowed to stir for 30 min at ambient temperature. When dichloromethane, acetonitrile, dioxane, ethyl acetate, or ether were used as solvents, the reaction was quenched by the addition of methanol containing NH$_3$ (equimolar amount to the catalyst), and the reaction mixture was evaporated to dryness under reduced pressure. In the cases of propylene carbonate PC, N,N-dimethylformamide DMF, N,N-dimethylacetamide DMAc, their reactions were quenched by addition of methanol containing NH$_3$, and the reaction mixture was poured into water to obtain precipita-

<p>| Table I. Cationic Polymerization of I in Nucleophilic Solvents |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent$^a$</th>
<th>DN$^b$</th>
<th>Temp (°C)</th>
<th>Conv.$^c$ (%</th>
<th>Yield.$^d$ (%)</th>
<th>$M_n$$^e$</th>
<th>$M_w/M_n$</th>
<th>Composition$^f$</th>
<th>Olefin content in polymer(mol%)$^g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_2$Cl$_2$</td>
<td>0</td>
<td>r.t.</td>
<td>100</td>
<td>0(100)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$CN</td>
<td>14.1</td>
<td>r.t.</td>
<td>100</td>
<td>40(32)</td>
<td>3100</td>
<td>2.51</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>Dioxane</td>
<td>14.8</td>
<td>r.t.</td>
<td>100</td>
<td>62</td>
<td>2700</td>
<td>67</td>
<td>33</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>PC</td>
<td>15.1</td>
<td>r.t.</td>
<td>92</td>
<td>72</td>
<td>3400</td>
<td>2.83</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>PC</td>
<td>15.1</td>
<td>0</td>
<td>87</td>
<td>64</td>
<td>5200</td>
<td>2.94</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$COOEt</td>
<td>17.1</td>
<td>r.t.</td>
<td>100</td>
<td>24(74)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>Ether</td>
<td>19.2</td>
<td>r.t.</td>
<td>67</td>
<td>18</td>
<td>3900</td>
<td>1.83</td>
<td>63</td>
<td>33</td>
</tr>
<tr>
<td>8</td>
<td>DMF</td>
<td>26.6</td>
<td>r.t.</td>
<td>34</td>
<td>14</td>
<td>1600</td>
<td>2.61</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>9</td>
<td>DMF</td>
<td>26.6</td>
<td>60</td>
<td>61</td>
<td>19</td>
<td>2800</td>
<td>4.46</td>
<td>68</td>
<td>32</td>
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<tr>
<td>10</td>
<td>DMAc</td>
<td>27.8</td>
<td>r.t.</td>
<td>27</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>11</td>
<td>Ethanol</td>
<td>32.6</td>
<td>r.t.</td>
<td>100</td>
<td>0$^h$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Polymerization was carried out for 30 min using 1 mol% of CF$_3$SO$_2$H.

$^b$ Monomer concentration = 0.5 mol/L.

$^c$ DN: donor number.

$^d$ Estimated from weight after evaporation of solvent.

$^e$ n-hexane-insoluble part, and crosslinked polymer in parentheses.

$^f$ Estimated by GPC. $^g$ Estimated by $^1$H NMR.

$^h$ Polymerization was carried out for 5 minutes.
ethylene acetate, and PC, were used, I was consumed almost quantitatively by addition of 1 mol% of CH₃SO₃H within 30 min to obtain the polymer in high yield. The results reveal that the preferential propagation by a certain particular functional group in cationic polymerization of multifunctional monomer becomes possible by addition of nucleophilic additive which interacts with the species responsible for cationic propagation to reduce its reactivity. The highest yield without crosslinking was observed in PC. In the cases of the solvents having higher DN value (>19.2), such as ether, DMF, and DMAc, (entry 7–10), lower conversion of I was observed because cationic species, responsible for propagation, are stabilized due to strong solvation, and polymerization occurred even in DMAc (DN = 27.8).

NMR and IR analyses of the polymers supported clearly that the desired polymer II was formed in every case, 4 and typical incorporation of solvents into the polymers could not be detected. Figure 1 shows the 1H NMR spectrum of the polymer obtained in DMF (entry 8). In every case, the ratio of units x and y estimated from 1H NMR was about 70:30, indicating the ratio of x and y depends on the nature of terminal allyl cation (Eq. 2) and is independent of the solvent.4 The intensities of NMR signals of olefinic protons were weaker than expected, indicating that intra-and intermolecular cationic side reactions involving the carbon-carbon double bonds in the main chain might occur as reported previously.4 Olefin content of the polymers increases slightly as the nucleophilicity of the solvent increases.

Results and Discussion

Cationic Polymerizations of I in Various Nucleophilic Solvents. Cationic polymerizations of I in various solvents, such as dichloromethane, acetonitrile, dioxane, PC, ethyl acetate, diethyl ether, DMF, DMAc, and ethanol, were carried out at ambient temperature using CF₃SO₃H as a cationic initiator. The results are summarized in Table I, and donor numbers (DN), 9 14 which is one of parameters representing the nucleophilicity of the solvents, are also stated in Table I. Although only crosslinked polymer was obtained in non-nucleophilic dichloromethane (DN=0), soluble polymers could be obtained even at ambient temperature in nucleophilic solvents except ethanol.

When the solvents having medium range of DN value (14.1–17.1), such as acetonitrile, dioxane,
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Figure 2. $^1$H-NMR spectrum of a reaction mixture of I and ethanol catalyzed by CH$_3$SO$_3$H (entry 10, Table I).

\[
\text{I} \xrightarrow{\text{K}} \begin{array}{c}
\text{III} \\
\text{IV} \xrightarrow{\text{EtOH}} \text{V} \xrightarrow{\text{H}} \text{VI}
\end{array}
\]

(Eq. 3)

in CDCl$_3$ in the presence of 1 mol% of CH$_3$SO$_3$H.

The conversion of I and the yield of polymer II increased as the reaction temperature was raised (entry 4, 5, and entry 8, 9). No crosslinked polymer was observed even at 60 °C in DMF. Thus, cationic polymerization of I at higher temperatures could be controlled effectively. The strong solvation of cationic intermediates III and IV may suppress undesirable side reactions such as crosslinking. Because of higher stability of oxallyl cation IV, cationic polymerization of I can proceed even in nucleophilic solvents.

Cationic polymerization has usually been carried out in non-nucleophilic solvents because nucleophilic solvents have been thought to inhibit cationic polymerization.$^1$ To establish unusual polymerizability of I, cationic polymerization of phenyl glycidyl ether, which is a typical cationically polymerizable monomer, was examined using CH$_3$SO$_3$H as an initiator but its polymerization in PC or DMF did not proceed at all.

**Cationic Polymerization of I in the Presence of Nucleophilic Compounds.** Cationic polymerizations of I with CF$_3$SO$_3$H in the presence of various nucleophiles, such as pyridine, amine, phosphine and ether, were carried out, and the results and pKa values of nucleophiles are summarized in Table II. In every case, only soluble polymer, II was obtained without crosslinking, and surprisingly, polymerization proceeded even in the presence of pyridine or triethylamine. The ratio of units x and y estimated from $^1$H NMR was about 70:30 in every case, indicating this ratio depended on the nature of terminal ally cation, and did not depend on the reaction condition.$^4$ Although cationic poly-

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Nu$^c$</th>
<th>pKa</th>
<th>Temp (°C)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
<th>$Mn$</th>
<th>$Mw/Mn$</th>
<th>Composition</th>
<th>Olefin content in polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF$_3$SO$_3$H</td>
<td>PhSCH$_3$</td>
<td>0.21$^c$</td>
<td>30</td>
<td>100</td>
<td>71</td>
<td>3600</td>
<td>2.21</td>
<td>67/33</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$SO$_3$H</td>
<td>PhSCH$_3$</td>
<td>0.21$^c$</td>
<td>30</td>
<td>100</td>
<td>71</td>
<td>3600</td>
<td>2.21</td>
<td>67/33</td>
<td>64</td>
</tr>
<tr>
<td>3</td>
<td>CF$_3$SO$_3$H</td>
<td>4-MP</td>
<td>6.00$^b$</td>
<td>30</td>
<td>18</td>
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<td>3600</td>
<td>2.04</td>
<td>67/33</td>
<td>60</td>
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<td>4-MP</td>
<td>6.00$^b$</td>
<td>30</td>
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<td>11</td>
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<td>67/33</td>
<td>60</td>
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<tr>
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<td>CF$_3$SO$_3$H</td>
<td>2-MP</td>
<td>5.96$^b$</td>
<td>30</td>
<td>31</td>
<td>19</td>
<td>4100</td>
<td>2.16</td>
<td>67/33</td>
<td>63</td>
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<tr>
<td>6</td>
<td>CF$_3$SO$_3$H</td>
<td>4-CN</td>
<td>1.92$^b$</td>
<td>30</td>
<td>71</td>
<td>41</td>
<td>2600</td>
<td>2.14</td>
<td>68/32</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>CF$_3$SO$_3$H</td>
<td>4-CN</td>
<td>1.92$^b$</td>
<td>5</td>
<td>56</td>
<td>29</td>
<td>2200</td>
<td>2.10</td>
<td>73/27</td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td>CF$_3$SO$_3$H</td>
<td>2-CN</td>
<td>0.26$^b$</td>
<td>5</td>
<td>100</td>
<td>61</td>
<td>3300</td>
<td>1.72</td>
<td>71/29</td>
<td>48</td>
</tr>
<tr>
<td>9</td>
<td>CF$_3$SO$_3$H</td>
<td>PPH$_3$</td>
<td>2.73$^c$</td>
<td>30</td>
<td>55</td>
<td>31</td>
<td>2400</td>
<td>1.66</td>
<td>68/32</td>
<td>65</td>
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<tr>
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<td>CF$_3$SO$_3$H</td>
<td>Dioxane</td>
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<td>100</td>
<td>58</td>
<td>3000</td>
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<tr>
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<td>Et$_2$O</td>
<td>-3.59$^b$</td>
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<td>100</td>
<td>67</td>
<td>2300</td>
<td>2.33</td>
<td>67/33</td>
<td>37</td>
</tr>
</tbody>
</table>

$^a$ Nucleophilic compound, MP: methylpyridine CN: cyanopyridine.

$^b$ Estimated by weight after evaporation of solvent.

$^c$ n-hexane-insoluble part. $^d$ Estimated by GPC.

$^e$ Estimated by $^1$H-NMR (mol%). $^f$ bimodal GPC curve.

$^g$ in H$_2$O, 25 °C, reference 10.


$^j$ In ethanol, reference 16. $^k$ in aqueous sulfuric acid, reference 17.


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merization of I with CF₃SO₂H or CH₃SO₂H in the absence of any nucleophile at ambient temperature gave only crosslinked polymers in dichloromethane, cationic polymerization of I with CF₃SO₂H in the presence of PhSCH₃ as a nucleophile afforded only soluble polymer II in 81% yield, whereas polymerization by CH₃SO₂H did not proceed. Thus, electrophilicity of CH₃SO₂H may be drastically reduced by the interaction with PhSCH₃ to be insufficient for the polymerization of I. Structure II could be confirmed by IR and "H NMR spectra, indicating that cationic polymerization of I by CF₃SO₂H in the presence of PhSCH₃ at ambient temperature took place in the same manner as that initiated by CH₃SO₂H in the absence of nucleophile at −78 °C. As shown in Figure 2 ("H NMR), incorporation of PhSCH₃ into the polymer could not be detected.

Conversion of the monomer clearly depended on the pKa of the nucleophiles. When nucleophiles with higher pKa were used, conversion decreased. Although 4-methylpyridine and 2-methylpyridine have similar pKa values, higher conversion could be obtained in the case of 4-methylpyridine since 2-methylpyridine is sterically more hindered. Thus, stronger interaction between nucleophiles and terminal cation may decrease its reactivity resulting in slower propagation and suppression of crosslinking. Olefin content of II was less than the theoretical value in every case, indicating the presence of side-reactions. Olefin content and Mw/Mn of II obtained by cationic polymerization in the presence of 4-cyanopyridine were plotted as a function of conversion of I as shown in Figure 3. Olefin content was almost constant (90%) until conversion approached to 50%, and gradually decreased when conversion was over 50%. Furthermore, noticeable change in value of Mw/Mn was not observed during polymerization.

These results suggested that an unclear intramolecular cyclization is a main side reaction, especially in the early stage of the polymerization. The olefin content increased when nucleophiles with higher pKa are used, indicating the reactivity of cationic intermediates III and IV decreased by the interaction with nucleophiles to surpress such side reactions.

Ring-opening polymerization of I in the presence of nucleophilic compounds gives a soluble polymer II in high yield even under relatively higher temperature. Nucleophiles could interact with cationic species to reduce their reactivity, resulting in quantitative transformation from III to IV and selective attack of enol ether part of monomer to IV. These idea may be applied to control various cationic polymerization system. This polymer can be useful reactive polymer.

References