Study of Photoinitiated Radical Copolymerization and Sequences of Acrylate-Vinyl Ether Systems

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Acrylate-vinyl ether copolymerization was analyzed by real-time FTIR, $^1$H and $^{13}$C NMR, confirmed that vinyl ethers were readily polymerized with acrylates in radical mechanism. Polymerization process of each monomer was monitored independently by real-time FTIR. While acrylate conversion was close to 100 %, vinyl ether conversion decreased as vinyl ether fraction in formulation increased. Conversion and copolymer compositions were determined by $^1$H NMR. It was found that any continuous vinyl ether sequences was not produced as a result of sequence analysis by $^{13}$C NMR as well as real time FTIR kinetics. $^{13}$C NMR study also indicated that propagating acrylic terminal was more reactive with vinyl ether monomer, than with acrylate.

**Keyword**: acrylate, vinyl ether, copolymerization, real-time FTIR, NMR

1. Introduction

Vinyl ethers are easily polymerized via photo-cationic initiation. In addition, it was noted that vinyl ethers may also undergo a radical copolymerization with monomers having an electron-deficient group, like maleimides, maleates or fumarates [1-3]. Vinyl ethers also radically copolymerize with acrylates. C. Decker and D. Decker analyzed photoinitiated radical copolymerization of polyether tetraacrylate-divinyl ethers systems by real-time FTIR [4]. The photocopolymer product was found to contain a large amount of unreacted vinyl ether’s double bond. This was explained by the lack of the tendency of vinyl ether’s homopolymerization, and acrylate radical’s two times higher reactivity toward the acrylate double bonds than toward the vinyl ether double bonds.

The kinetics of these radical photopolymerizations and the structural properties of the resulting polymers have been investigated extensively. Though acrylates polymerize rapidly and are extensively modified at the ester functionality, allowing access to materials with a variety of properties, these present a potential safety hazard when these are relatively low molecular weight.

Though vinyl ethers are attractive due to its less skin irritant and less viscous as compared with same size acrylates, cationically polymerizable system for vinyl ether system has drawbacks mainly due to photocationic initiators; their ionic character, toxicity, cost, etc. For that matter, acrylate-vinyl ether photo-copolymerizations mediated by radical chemistry would have potentially-useful processes.

In this paper, we report a study of photoinitiated radical acrylate-vinyl ether copolymerization determined by real-time FTIR, conversion and copolymer compositions by $^1$H NMR, and sequences by $^{13}$C NMR.

2. Experimental section

2.1 Materials

UV-curable formulation contains acrylates: benzyl acrylate (BZA, Hitachi Chemical) and neopentyl glycol diacrylate (NPG-DA, Shin-Nakamura Chemical), and vinyl ethers: tricyclodecane monomethanol vinyl ether (TMM-VE, Maruzen Petrochemical) and diethylene glycol divinyl ether (DEG-DVE, Aldrich).

2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propane-1-one (Irgacure 907, Ciba) was used
as a radical photoinitiator. (4-methylphenyl)[4-(2-
methylpropyl)phenyl]-hexafluorophosphate(1-)iodonum (Irgacure 250, Ciba) was used as a cation
photoinitiator with a photosensitizer 9-methyl-
anthracene (9-MeAn, Tokyo Chemical Industry).

All reagents were used as received without any
further purification.

2.2 Sample preparation

Photoinitiator was weighted in a 10 mL screw
vial, and the acrylate and vinyl ether were added.
The vials were stirred so that no solid remained in
the solution.

2.3 Real-time FTIR

The experimental setup is illustrated in Figure
1. The sample solution was dropped on a silicon
wafer and covered with CaF
2
to keep out oxygen
diffusion from air and to avoid sagging. Sample
holder was tilted 45 degree against UV and IR.

Real-time FTIR spectra were recorded using a
DIGLAB FTX3000MX FTIR spectrometer
(spectral resolution of 2 cm
-1
). UV irradiation was
performed with an USHIO SP-7 with an Asahi
Spectra 365 nm bandpass filter. An electronic
shutter DIGLAB Trigger interface K001 controlled
by the spectrometer computer enabled the
synchronization between the UV exposure and the
IR spectra recording.

Spectra were recorded for 180s. The sample
was irradiated for 25s and then the shutter was
closed until the end of the measurement. All
irradiations were performed at light intensity of 5
mW·cm
-2
. But sample was tilted 45 degree, light
intensity irradiated sample was corrected to 3.5
mW·cm
-2
.

Double bonds in acrylates absorb at 1415 cm
-1
.
Therefore, the acrylate double bond conversion
was calculated by monitoring the peak height at
1415 cm
-1
. The vinyl ether conversion was
calculated by monitoring the peak height at 1322
cm
-1
. Peak at 1322 cm
-1
was estimated to be C-O-C
antisymmetric stretching, which was characteristic
of vinyl ether in this paper.

2.4 \textsuperscript{1}H and \textsuperscript{13}C NMR

Approximately 100 mg of sample was put into
a quartz cell with a light path of 5 mm. The cell
purged with N
2
gas to prevent oxygen diffusion
from air, and capped with PARAFILM. Then,
sample was exposed to UV light. UV irradiation
was performed with an USHIO spot cure SP-7 with
an Asahi Spectra 365 nm bandpass filter. Light
intensity was 10 mW·cm
-2
, irradiation time was
100s.

NMR analyses were performed on a Bruker
BioSpin AV400M spectrometer at room
temperature using CDCl
3
as a solvent and
tetramethylsilane (TMS) as an internal standard.
UV irradiated sample and 0.2 mg of TMS were
dissolved in 0.5 ml of CDCl
3
.

\textsuperscript{1}H NMR spectroscopy was used to determine
copolymer compositions. Spectra were recorded at
room temperature operating at 400.23MHz.
Typical parameters for the proton spectra were 5 μs,
width 30 μ, pulse delay 2s, acquisition time of 4.1s,
and 16 scans.

Sequences of the copolymers were studied by
\textsuperscript{13}C NMR, recorded at room temperature with the
same spectrometer operating at 100.648 MHz at
with complete proton decoupling techniques. The parameters for carbon spectra were the flip angle
of 30 μ (pulse width 2.8 μs), delay time 2s, and
15000 scans. The signal intensities of spectra peaks
were measured from the integrated peak areas
calculated with an electronic integrator.

3. Results and Discussion

3.1 Polymerization monitoring by real-time
FT IR

Acrylate-vinyl ether copolymerizations at
different formulation were carried out shown in
Table 1.

<p>| Table 1. Formulation of samples (1) (mol%). |</p>
<table>
<thead>
<tr>
<th>Sample No\textsuperscript{*}</th>
<th>BZA</th>
<th>TMM-VE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

*All samples contained 5 weight parts Irgacure 907.

Figure 2 shows the polymerization profiles of
acrylates and vinyl ethers in sample recorded by
real-time IR upon UV exposure. Any
polymerization did not occur in Sample 5. But in
sample 2 to 4, vinyl ether underwent radical
polymerization with acrylate. As the fraction of vinyl ether in sample increased, the conversion of vinyl ether decreased.

3.2 Study of photoinitiators

Acrylate-vinyl ether copolymerizations with radical, cation, or hybrid photoinitiators were carried out, as shown in Table 2. Polymerization recorded by real-time FTIR was shown in Figure 3.

From these results, it was supposed the mechanism illustrated in Scheme 1. While acrylate radical attacks both to acrylate and vinyl ether, vinyl ether radical attacks only to acrylate monomers. When the ratio of vinyl ether is high, vinyl ether radical cannot react because only vinyl ether monomer remains. This was also depicted in previous report [4].

Scheme 1. Acrylates and vinyl ethers radical copolymerization

Figure 2. Acrylate and vinyl ether conversion vs. exposure dose

Figure 3. Acrylate and vinyl ether conversion vs. exposure dose
Table 2. Formulation of samples (2) (mol%).

<table>
<thead>
<tr>
<th>Sample No</th>
<th>r-1</th>
<th>r-2</th>
<th>r-3</th>
<th>c-1</th>
<th>c-2</th>
<th>c-3</th>
<th>rc-1</th>
<th>rc-2</th>
<th>rc-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPG-DA</td>
<td>100</td>
<td>40</td>
<td>0</td>
<td>100</td>
<td>40</td>
<td>0</td>
<td>100</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>DEG-DVE</td>
<td>0</td>
<td>60</td>
<td>100</td>
<td>0</td>
<td>60</td>
<td>100</td>
<td>0</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Irgacure 907(^1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irgacure 250(^2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9-MeAn(^3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) 5 weight parts Irgacure 907 added to monomers. 2) 1 weight parts Irgacure 250 added to monomers. 3) 0.1 weight parts 9-MeAn added to monomers.

In sample c-2, as the conversion of vinyl ether was 100%, NPG-DA was consumed about 20%. Diarylindonium salt generates radicals via photoinduced electron transfer from an excited photosensitizer [5]. In rc-1, rc-2 as a hybrid system, polymerizations were similar to them in radical system except that reaction rates were slower than c-1 and c-2. Unexpectedly in sample rc-3, no polymerization occurred.

3.3 Copolymers conversion by \(^1\)H NMR

The photo-products for the samples shown in Table 1 were subjected to \(^1\)H NMR analyses without any purification. \(^1\)H NMR spectra of sample 1-5 are showed in Figure 4.

Figure 4. \(^1\)H NMR spectra of A-V copolymers

Four peaks were used to calculate the conversion of photopolymerization. The peak of 7.2 ppm was assigned to five protons of aromatic ring in acrylate. This peak derived both of acrylate monomer and polymer, indicating the total acrylate. The peak of 6.2 ppm was assigned to one proton of \(-\text{CH}_2\) in acrylate monomer, indicating unreacted acrylate.

Structure of BZA monomer.

![Structure of BZA monomer.](image)

The peak of 0.9 ppm assigned to one proton of tricyclicdecane moiety of vinyl ether illustrated in Figure 6. This peak shifted to 0.7 ppm when TMM-VE turns to its polymer.

Structure of TMM-VE monomer.

![Structure of TMM-VE monomer.](image)

From above peaks’ area, the conversions of acrylates and vinyl ethers were calculated. The result is showed in Table 3.

Table 3. Conversion measured by \(^1\)H NMR (%).

<table>
<thead>
<tr>
<th>Sample No</th>
<th>A</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>99</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>96</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>12</td>
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<tr>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Fractions of acrylate and vinyl ether in copolymer were also calculated from each conversion, and are showed in Table 4.
Table 4. Copolymer compositions (%).

<table>
<thead>
<tr>
<th>Sample No</th>
<th>A</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>68</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Calculated by conversion data in Table 3.

3.4 Sequences of the copolymers by $^{13}$C NMR

$^{13}$C NMR spectra for UV irradiated sample 1-4 suggested that the well-controlled head-to-tail structure of the copolymer was given. To analyze sequences, there are two possible peaks which correspond to acrylate centered triads in $^{13}$C NMR spectra; the peak around 174 ppm was assigned to carbonyl carbon and the peak around 36 ppm was assigned to -CH$_2$- of polymerized acryloyl group. Since the peak at 36 ppm overlaps to the peak of TMM-VE, the peaks appeared in 173.5-176.5 ppm of spectra of sample 1-4 were subjected to sequence analyses. Figure 5 shows the carbonyl carbon signals for the copolymer compositions. There are three distinguishable signals which change drastically with copolymer composition.

The peaks of 174.0-174.5 were assigned to AAA triad; the peaks of 174.5-175.0 ppm to AAV (and VAA) triad, and the peaks of 175.0-176.0 ppm to VAV triad.

The ratios of three acrylate centered triads were calculated derived from the peak areas. Results were summarized in Table 5. Results of the calculated sequences using obtained copolymer compositions, assuming that continuous vinyl ether sequences were not produced and the reaction rates of acrylate and vinyl ether were the same, also showed in Table 5.

![Figure 5](image)

**Figure 5** $^{13}$C NMR spectra (177-173 ppm)

The peaks appeared around 73.0-76.0 ppm in $^{13}$C NMR spectra of sample 2-4 were assigned to -CH$_2$- of polymerized vinyl ether as shown in Figure 6. It was elucidated that these peaks’ splitting were reflected only by tacticity, not sequences, since these peaks’ area does not have any relation to copolymer compositions derived from $^1$H NMR. Considering that no polymer was produced, the peaks appeared in 73-76 ppm of sample 1-4 probably were assigned only to the AVA triad as vinyl ether centered sequence.

![Figure 6](image)

**Figure 6** $^{13}$C NMR spectra (77-72 ppm)
Table 5. Sequences of acrylate centered determined by $^{13}$C NMR(\%).

<table>
<thead>
<tr>
<th>Sample No</th>
<th>AAA</th>
<th>AAV (VAA)</th>
<th>VAV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated*</td>
<td>Experimental</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>58</td>
<td>72</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>37</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>19</td>
<td>33</td>
</tr>
</tbody>
</table>

*Calculations were performed on the assumption that continuous vinyl ether sequences were not produced, and reaction rates of acrylate and vinyl ether monomer were same.

The fraction of AAA triad in the copolymer was smaller than expected by calculation in sample 2-4. On the contrary, the fraction of VAV triad in the copolymer was more than expected. It seems that the AAV (VAA) triad has a tendency to decrease as the vinyl ether in polymer increase.

Continuous acrylate sequences were seen fewer than expected. This result indicated that the acrylate propagating terminal was more reactive with the vinyl ether, than with the acrylate.

4. Conclusion

Using real-time FTIR, $^1$H NMR and $^{13}$C NMR, copolymerization of acrylates and vinyl ethers was studied, and the followings were concluded.

Vinyl ethers rapidly copolymerize with acrylates via radical chemistry under UV irradiation. But there remains vinyl ether unreacted as the fraction of vinyl ethers in the system increase, consisting with previous knowledge [4]. This was endorsed by the sequences analyses, showing that propagating acrylic terminal is more reactive with vinyl ether, than with acrylate.

References