Effect of Spacer Unit on Photo-Initiated Thermal Crosslinking of Polyomers Having Carbamoyloxyimino Groups in Side-Chains

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Carbamoyloxyimino (COI) groups are known to generate amino groups photochemically and isocyanato groups thermally, and these generated groups have been used for highly efficient crosslinking systems. In this article, a series of polymers which were connected to COI groups with or without spacer units were prepared, and their crosslinking behavior on irradiation followed by heating was investigated to clarify the effect of the length of side-chain. There was no effect of spacer units on photoreactivity of COI groups. On the other hand, thermal reactivity of COI groups in polymers with spacer unit was faster than that in polymers without spacer unit. Thermogravimetric analyses and real-time IR spectroscopy revealed lower thermal decomposition temperature, lower glass transition temperature, and higher thermal decomposition rate of COI groups in copolymers with spacer unit compared to corresponding polymers without spacer unit. These behaviors were reflected on the crosslinking on irradiation followed by heating, where films of polymers with spacer unit showed more effective insolubilization than those without spacer unit. Other factor such as comonomer and the presence of α-methyl group on main-chain were also investigated.

Keywords: oxime carbamate; post-exposure bake; blocked isocyanate; crosslink; photobase generator; side-chain

1. Introduction

The formation of crosslinks in polymers gives drastic changes of their mechanical and thermal properties as well as their chemical resistance. These changes can be used in many applications, especially in the fields of coating and photolithographic technologies.

In many crosslinking systems, reactive functional groups are often introduced into polymer side-chains. In these systems, higher mobility of the groups is advantageous for faster crosslinking. However, there are not so many reports that investigate the effect of length of side-chains between the reactive groups and main-chains, although it will affect the mobility.

In this article, we report the effect of spacer units between the reactive carbamoyloxyimino (COI) groups and main-chain on their photo- and thermal reactivity, and crosslinking behavior as illustrated in Fig. 1. It has already known that COI groups are transformed into basic (amino and hydrazino) groups on UV-irradiation [1-3] and isocyanato groups on heating [4,5] as shown in Scheme 1. Also, the generation of both the basic and isocyanato groups from COI groups has already been applied in highly sensitive crosslinking systems [6-12].

Fig. 1. Crosslinking of polymers bearing photo- and thermolabile groups with different length of side-chains.
Scheme 1. Photo- and thermal reactions of O-carbamoyloximes.

We have prepared new monomers bearing COI groups with different length of side-chains and polymerized them to obtain a series of polymers in Fig. 2. Using these polymers, the effect of spacer unit between COI group and main-chain, comonomer, and α-methyl groups on main-chain on the photo-reactivity, thermal reactivity, and crosslinking is examined and discussed.

2. Experimental

Melting point was measured by a Yanako MT-3S micro melting point meter and uncorrected. IR, UV, and NMR spectra were obtained using Jasco FIR-410, Shimadzu UV-2400PC, and Jeol JNM-LA400 (400 MHz) spectrometers, respectively. Elemental analysis was performed using a Yanagimoto MT-3 CHN corder. Dibutyltin dilaurate, 1-dodecanethiol, 2,6-di-tert-butyl-p-cresol, dinitrobenezene, 2-(methylacryloyloxy)ethylisocyanate (Showa Denko), and 2-(acyrlyloxy)ethylisocyanate (Showa Denko) were used as received. 2,2'-Azobisisobutylonitrile (AIBN) was recrystallized from diethyl ether. Methyl methacrylate (MMA), methacrylonitrile (MAN), N,N-dimethylformamide (DMF) were distilled under reduced pressure, and ethyl acetate, diethyl ether, and tetrahydrofuran (THF) were distilled before use.

Acetophenone O-methacryloyloxyethylcarbamoyloxime (AMCO, mp: 54-54.5 °C) [3] and 2-acetonaphthone O-methacryloyloxyethylcarbamoyloxime (NMCO, mp: 91-92 °C)[13] were obtained as described previously.

Acetophenone O-acryloyloxyethylcarbamoyloxime (AACO): In a flask equipped with a septum and a CaCl₂ tube, 1.65 g (12.2 mmol) of acetophenone oxime, a bit of 2,6-di-tert-butyl-p-cresol, a drop of dibutyltin dilaurate, and 5.0 ml of ethyl acetate were placed. The flask was cooled in an ice bath, and 1.5 ml (11.6 mmol) of 2-(acryloyloxy)ethylisocyanate was added dropwise through the septum over 20 min. Then, the mixture was stirred for 15 h in the ice bath. After removal of ethyl acetate with a rotary evaporator, obtained white solid was recrystallized from diethyl ether to afford 2.05 g of colorless needles: yield 63.4 %, mp 37.5 – 38 °C, ¹H NMR (CDCl₃): δ = 2.44 (3H, s, CH₃), 3.65 (2H, q, NHCH₂), 4.34 (2H, t, J = 5.4 ppm, COOCH₂), 5.87 (1H, d, trans CH₂=), 6.14 (1H, dd, J = 10.5 and 17.3 Hz, CH), 6.45 (1H, d, cis CH₂=), 6.79 (1H, broad s, NH), 7.40-7.50 (3H, m, meta and para), 7.67-7.70 (2H, m, ortho). Caled for C₁₄H₁₈N₂O₄: C 60.86, H 5.84, N 10.14. Found: C 61.13, H 5.91, N 9.88.

Vinyl isocyanate and 2-propenyl isocyanate were prepared from sodium azide and acryloyl chloride and methacryloyl chloride, respectively, via Curtius rearrangement as described in literature [14]. In both cases, the crude products were distilled twice, and the formation of the products was checked by¹H NMR measurement.

Acetophenone O-vinylcarbamoyloxime (AVCO) was obtained by adding 2.10 ml (30.9 mmol) of freshly distilled vinyl isocyanate to the solution consisting of 4.10 g (30.9 mmol) of

![Fig. 2. Polymers examined in this study.](image-url)
acetophenone oxime, a few drops of dibutyltin dilaurate, 0.06 g of dinitrobenzene, and 3.20 ml of ethyl acetate in a flask in ice bath. After stirring for 43 h in dark at room temperature, the solution was passed through silica gel column, and evaporated. The resulting solid was recrystallized from hexana: ethanol = 9:1 (v/v) solution to afford 5.17 g of colorless crystals: yield 83.8 %, mp = 89 - 89.5 °C. IR (KBr): 1730 cm⁻¹ (ester C=O), 3400 and 1505 cm⁻¹ (NH). ¹H NMR (CDCl₃): δ = 2.45 (3H, s, CH₃), 4.47 (1H, d, J = 8.9 Hz, trans CH₂=), 4.69 (1H, d, J = 15.8 Hz, cis CH₂=), 6.77-6.90 (1H, m, CH=), 7.42-7.49 (3H, m, meta and para), 7.66-7.70 (2H, m, ortho), 8.05 (1H, broad s, NH). ¹³C NMR (CDCl₃): δ = 14.78, 95.90, 126.85, 128.77, 129.18, 130.84, 134.51, 152.73, 161.22. Calcul for C₁₄H₁₅N₂O₄: C 64.69, H 5.92, N 13.72. Found: C 64.55, H 5.88, N 13.81.

2-Acetonaphthone N-vinylcarbamoyloxyime (NVCO) was obtained by adding 1.88 g (34.9 mmol) of vinyl isocyanate to the solution consisting of 4.73 g of acetophenone oxime (25.5 mmol), a few drops of dibutyltin dilaurate, 0.06 g of dinitrobenzene, and 70 ml of chloroform in a flask in ice bath. After stirring for 39 h in dark at room temperature, the solution was passed through silica gel column, and evaporated. The resulting solid was recrystallized from hexana-ethanol mixed solution to afford 5.70 g of yellowish powder: yield 86.2 %, mp = 89-90 °C. ¹H NMR (CDCl₃): δ = 2.57 (3H, s, CH₃), 4.49 (1H, d, J = 8.9 Hz, trans CH₂=), 4.76 (1H, d, J = 15.8 Hz, cis CH₂=), 6.80-6.93 (1H, m, CH=), 7.52-8.11 (8H, m, aromatic and NH). Calcul for C₁₁H₁₂N₂O₂: C 70.85, H 5.55, N 11.02. Found: C 71.15, H 5.83, N 10.86.

Acetophenone O-(2-propenyl)carbamoyloxyime (APCO) was obtained by adding 4.0 g (48 mmol) of 2-propenylisocyanate to the solution consisting of 6.42 g of acetophenone oxime (47.5 mmol), a few drops of dibutyltin dilaurate, small amount of tert-butylcatechol, a few bits of molecular sieves, and 4.2 ml of ethyl acetate in a flask in ice bath. After stirring for 43 h in dark at room temperature, the solution was filtered and evaporated. To the aliquot, 80 ml of chloroform was added, and the solution was washed with water three times. After drying with sodium sulfate, the solvent was removed by evaporation to afford 11 g of viscous tar. After purification of 1.5 g of the tar with silica gel column chromatography using chloroform as an eluent, 1.4 g of APCO was obtained as colorless tar. Yield 13 %. ¹H NMR (CDCl₃): δ = 1.99 (3H, m, C=CH₂), 2.41 (3H, m, N=C=CH₂), 4.48 (1H, s, CH=), 5.27 (1H, s, CH=), 7.39-7.67 (5H, m, aromatic). Calcul for C₁₄H₁₆N₂O₄: C 66.02, H 6.47, N 12.84. Found: C 65.80, H 6.20, N 12.82.

Monomers, AIBN, and DMF were put in a tube, argon-bubbled for 20 min, and heated at 60 °C. After the heating, the solution was poured into methanol, and the resulting solid was reprecipitated three times from methanol after dissolving in THF. A homopolymer of MAN (PMA) was obtained by polymerization initiated by AIBN followed by reprecipitation: Tg 70 °C.

The molar fraction of monomers incorporated in the copolymers was determined by elemental analysis. The molecular weights were measured by size exclusion chromatography (SEC) at 40 °C on a Jasco GPC equipment consisting of a PU-980 pump, an RI-930 and a Shodex KF-806M column with polystyrene as standard and tetrahydrofuran (THF) as eluent.

Glass transition temperature (Tg) was obtained by a Shimadzu DSC-60 differential scanning calorimeter at a heating rate of 10 K/min under N₂. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA50 analyzer. Polymerization conditions and characterization of purified polymers were listed in Table 1.

Films were prepared by casting their cyclohexanone solution onto silicon or quartz plates using a spin coater. Films were pre-baked at 60 °C for 2 min on a Koike Precision Instruments HM-15G hot plate. The thickness of films on silicon plates was measured by a Nanometrics Nanospec/AFT M3000 interferometer.

Real-time infrared spectroscopy (RT-IR) was carried out on a Lithotech PAGA100. The first scan was omitted because of great changes of baseline. For the generation of isocyanate groups, the ratio of absorbance at 2275 cm⁻¹ (A₂₂₇₅) against that at 1505 cm⁻¹ before irradiation (A₁₅₀₅) was used.

Irradiation was carried out with an Ushio ULO-6DQ low-pressure mercury lamp (6 W) at room temperature in air. Light intensity at 254 nm was 1.0 mW/cm², which was measured by an Orc UMK-02 photoluminometer. Post-exposure bake (PEB) was carried out on the hot plate for 10 min in air.

Development was performed by soaking the irradiated films in THF for 10 min at room
Table 1. Polymerization conditions and characteristics of polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>COI monomer (mol%) in feed</th>
<th>DMF monomer (wt%)</th>
<th>AIBN (wt%)</th>
<th>P. T. (h)</th>
<th>Conv. (%)</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>$T_g$ (°C)</th>
<th>$T_d$ (°C)</th>
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<tr>
<td>AVCO-MMA</td>
<td>30</td>
<td>39</td>
<td>1.0</td>
<td>1.0</td>
<td>5</td>
<td>35</td>
<td>47,000</td>
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<td>93</td>
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<tr>
<td>AMCO-MMA</td>
<td>30</td>
<td>24</td>
<td>1.0</td>
<td>0.35</td>
<td>0.4</td>
<td>66</td>
<td>9,500</td>
<td>1.25</td>
<td>64</td>
</tr>
<tr>
<td>AVCO-MAN</td>
<td>30</td>
<td>49</td>
<td>1.0</td>
<td>1.0</td>
<td>10</td>
<td>17</td>
<td>8,400</td>
<td>1.78</td>
<td>107</td>
</tr>
<tr>
<td>AMCO-MAN</td>
<td>30</td>
<td>44</td>
<td>1.5</td>
<td>1.0</td>
<td>12</td>
<td>18</td>
<td>24,000</td>
<td>2.19</td>
<td>65</td>
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<tr>
<td>NVCO-MAN</td>
<td>30</td>
<td>45</td>
<td>1.0</td>
<td>1.0</td>
<td>33</td>
<td>55</td>
<td>11,000</td>
<td>2.01</td>
<td>127</td>
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<tr>
<td>NMCO-MAN</td>
<td>30</td>
<td>54</td>
<td>1.0</td>
<td>1.0</td>
<td>13</td>
<td>41</td>
<td>9,000</td>
<td>1.65</td>
<td>79</td>
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<tr>
<td>PAACO</td>
<td>100</td>
<td>100</td>
<td>6.0</td>
<td>1.0</td>
<td>3.5</td>
<td>68</td>
<td>2,700</td>
<td>1.76</td>
<td>49</td>
</tr>
<tr>
<td>PAMCO</td>
<td>100</td>
<td>100</td>
<td>6.0</td>
<td>1.0</td>
<td>10</td>
<td>55</td>
<td>4,300</td>
<td>1.86</td>
<td>71</td>
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</tbody>
</table>

a) From elemental analyses. b) Against monomer. c) Polymerization time. d) After reprecipitation. e) From SEC with polystyrene standards. f) From DSC. g) On set temperature from TGA. h) Polymerization was carried out in the presence of 1-dodecanethiol (10 wt% against total monomers) to avoid gelation.

temperature. Normalized film thickness of polymer films was obtained from ratios of thickness before and after the soaking. Thickness of films before soaking was 0.4–0.7 μm.

3. Results and Discussion

3.1 Preparation of copolymers bearing COI groups

Monomers bearing COI groups including new compounds AACO, AVCO, APCC, and NVCO shown in Fig. 3 were prepared by addition reaction of corresponding isocyanates and oximes. These monomers were copolymerized with methacrylonitrile and methyl methacrylate except APCC and AACO. In case of APCC, neither homopolymer nor copolymer was obtained, even though the disappearance of double bonds was confirmed by $^1$H NMR measurement. From AACO, only homooligomer was obtained. Thus, we also prepared an oligomer of AMCO in order to investigate the effect of α-methyl group on main-chain. Physical properties of polymers are listed in Table 1.

Typical TGA profiles are shown in Fig. 4. For AMCO-MAN and AVCO-MMA, the first weight loss was almost identical to the weight fraction of acetoephone unit in each copolymer, 36 and 37 %, respectively, suggesting that acetoephone oxime vaporized after thermal decomposition of COI groups. However, this tendency was not observed for AVCO-MAN. AMCO-MMA did not show clear two step weight loss.

As shown in Table 1, $T_d$ and $T_g$ for AMCO-MAN and AMCO-MMA having spacer units were lower than those of AVCO-MMA and

![Chemical structure](attachment:image.png)

Fig. 3. Monomers bearing COI groups.

AVCO-MMA, respectively. NMCO-MAN showed a lower $T_g$ than NVCO-MAN, but similar $T_d$, probably due to slow evaporation of generating 2-acetonaaphthone oxime.

3.2 Photoreactivity of COI groups in side-chain

Figure 5 shows UV spectral changes of AVCO-MAN and NVCO-MAN films on irradiation. In both cases, the peaks around 250 nm due to COI groups decreased with an increase of irradiation energy. Similar spectral changes were observed for all polymers, and the reaction rates for NVCO-MAN and NMCO-MAN were faster than those of the other polymers.

IR spectral changes also show the photolysis of COI groups. Typical IR changes are shown in Fig. 6 for AVCO-MAN films, where peaks at 1505 and 1730 cm$^{-1}$ due to N-H wagging and C=O stretching bands in COI units, respectively,
Fig. 4. TGA profiles for copolymers of a) MAN and b) MMA copolymers with AVCO (solid line) and AMCO (dashed line) with heating rate at 5 K/min under N₂. Numbers in figures show the weight fractions of acetophenone oxime units in the copolymers.

decreased with an increase in irradiation energy. These changes suggest the formation of pendant amino and hydrazino groups from the previous studies using model compound.[9] Similar IR spectral changes were observed for all polymers.

Based on the changes of peak intensity at 1505 cm⁻¹, the degree of photolysis of COI groups in some polymers is plotted against irradiation energy in Fig. 7. Although there was slight variation in the rate of photolysis of COI groups, the rates were almost identical for these polymers, suggesting that the photoreactivity of COI groups was independent on the length of side-chains, and kind of comonomers. The rate for NMC-MAN and NVCO-MAN films could not be evaluated from IR because they have strong absorbance at 254 nm, and the peak intensity at 1505 cm⁻¹ was too small to analyze if we use thinner film whose

Fig. 5. UV spectral changes of a) AVCO-MAN and b) NVCO-MAN films on irradiation at 254 nm. Numbers in the figure show irradiation energy. Film thickness: a) 0.5 μm, b) 0.1 μm.

Fig. 6. IR spectral changes of AVCO-MAN films on irradiation at 254 nm. Numbers in the figure show irradiation energy and wavenumbers at peak tops. Film thickness: 0.7 μm.
absorbance at 254 nm was less than 1.

3.3 Thermal reactivity of COI groups in side-chain

RT-IR spectral change for AMCO-MAN film on heating is shown in Fig. 8. In addition to the decrease of peaks at 1760, and 1505 cm⁻¹ that was observed on irradiation, a new peak appeared at 2275 cm⁻¹ due to isocyanato groups. These changes of peaks were also observed for other polymers on heating.

The decrease of COI groups on heating was plotted in Fig. 9a. COI groups in AMCO-MAN and NMCO-MAN decomposed faster than those in AVCO-MAN and NVCO-MAN, respectively, and the rate for AMCO-MMA was slightly faster than that for AVCO-MMA. Copolymers containing naphthyl units decomposed slower than those containing phenyl groups.

The generation of isocyanato groups was compared in Fig. 9b [15], where AVCO-MMA, AVCO-MAN, and NVCO-MMA showed higher degree of generation than AMCO-MMA, AMCO-MAN, and NMCO-MMA, respectively, at longer heating time.

These results in Fig. 9 showed that polymers bearing COI groups with spacer units showed higher rates of decomposition of COI groups and generation of isocyanato groups than those without spacer units. These results were consistent with thermal properties discussed in section 3.1.

The effect of α-methyl group on main-chain was investigated by comparing PAAO and PAMCO in Fig. 10, showing the effect was negligible.

Concerning to comonomer, copolymers of MMA showed much higher decomposition rate than those of MAN as shown in Fig. 9a. This tendency was also confirmed in Fig. 10, where the thermal decomposition rate of COI groups decreased in the order PAMCO > PAMCO blended with PMAN > AMCO-MAN. These results indicated that the introduction of MAN unit afforded slower thermal decomposition.

Fig. 8 RT-IR spectra for AMCO-MAN films on heating at 150 °C. Numbers in the figure shows wavenumbers at peak tops.
3.4 Solubility changes of polymer films

Films of copolymer were almost soluble in THF even after irradiation and became insoluble due to crosslinking between photochemically generated basic groups and thermally generated isocyanato groups. Figure 11a shows that AMCO-MAN and AVCO-MAN films became insoluble in THF on irradiation followed by heating at 120 °C, and the former was faster than the latter. As shown in Fig. 11b, films of AMCO-MMA and NMCO-MAN showed higher degree of insolubilization than those of AVCO-MMA and NVCO-MAN, respectively, after heating at 130 °C for 5 min. These results show the same tendency for thermal reactivity of COI.
groups as described in section 3.3, showing the advantage of copolymers having spacer units. AMCO-MAN and AVCO-MAN films became insoluble on heating at 130 °C even without irradiation, although thermal decomposition of COI groups was slower compared to corresponding copolymers of MMA. PAMCO films became insoluble with smaller irradiation energy than other copolymers as shown in Fig. 12, probably due to high density of COI groups. PAACO films became insoluble only on heating.

4. Conclusions

Several polymers bearing COI groups were prepared, and their photochemical and thermal reactivity, and crosslinking behaviour was compared. The effect of spacer unit between main-chain and COI group was not observed on photoreactivity, but clearly observed for the formation of isocyanato groups on heating. This tendency was also observed for crosslinking on irradiation followed by heating. Polymers having naphthyl groups showed higher photoreactivity and thus needed less irradiation energy for crosslinking on irradiation followed by heating. The effect of comonomer was complicated, where MAN copolymers showed slow thermal decomposition but faster crosslinking behaviour than corresponding MMA copolymers. The effect of α-methyl groups on main-chain was negligible on photo- and thermal reactivities.

Authors acknowledge to Showa Denko for providing 2-(methacryloyloxy)ethylisocyanate, 2-(acryloyloxy)ethylisocyanate, and 2-butanone O-methacryloyxoyethylcarbamoyloxime.

5. References

15. First we tried to decompose COI groups completely on heating at 200–210 °C, but failed because generated isocyanato groups in most polymers degraded rapidly at this temperature. For AMCO-MMA film, it was confirmed that the maximum value of $A_{2270}/A_{1805/3-0}$ was 1.9, which was obtained on heating at 200 °C for 1 min. This value was almost identical to that obtained on heating for 1150 s in Fig. 9b. Therfore, we used this parameter here.