

# Structural Characterization of Photocured Acrylic Resins Using Specific Decomposition Reactions

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Chemical structures of photocured acrylic ester resins were characterized using specific decomposition techniques such as pyrolysis-gas chromatography in the presence of organic alkali and matrix-assisted laser desorption/ionization mass spectrometry combined with super critical methanolysis. The resultant products formed through specific cleavage at the ester linkages in the cured resin samples were interpreted in terms of copolymer composition; average molecular weight of the original prepolymers; double

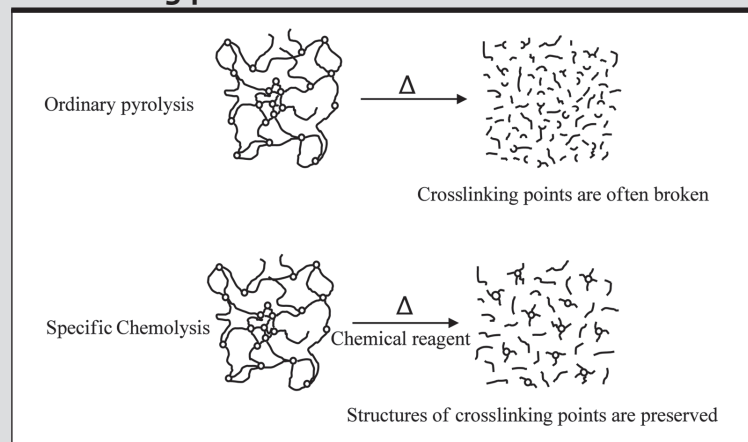
bond conversions; and distributions in crosslinking sequences.

Structural characterization of the crosslinking network structure in the photocured resins has not been an easy task—even when using advanced spectroscopic methods—mainly because of their insoluble nature. Meanwhile, pyrolysis-gas chromatography (Py-GC) has been utilized for investigating the chemical structure of various polymeric materials, even for insoluble ones. However, as shown in Figure 1, ordinary pyrolysis often causes unspecific decomposition of the crosslinking polymer samples in which various structural information might also be lost. On the other hand, in the case of thermally assisted chemolysis, specific decomposition of the sample materials can be achieved while preserving the structural information of the crosslinking networks.

In this work, the chemical structure of ultraviolet (UV)-cured acrylic resins were characterized using a specific sample decomposition procedure (such as pyrolysis-gas chromatography) in the presence of organic alkali and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) combined with supercritical methanolysis. Figure 2 shows a typical model of the specific

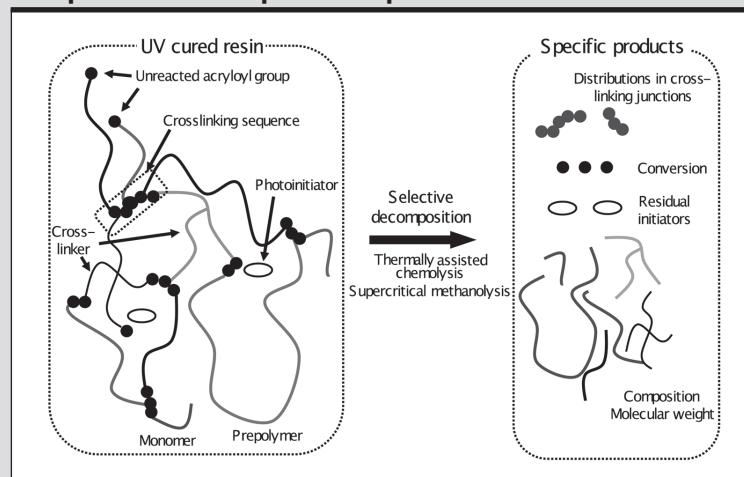
FIGURE 1

## Model scheme of ordinary pyrolysis and specific chemolysis with preserving structures of crosslinking point



## FIGURE 2

## Model structure of UV-cured acrylic ester resin and its specific decomposition products



decomposition of the UV-cured acrylic resin. From the obtained fragments, some valuable information for conversion, residual initiator, composition and molecular weight of original monomer/prepolymer, and distribution in crosslinking junctions can be obtained.

## Characterization by Py-GC in the Presence of Organic Alkali

Figure 3 shows the schematic diagram of reactive Py-GC system in the presence of an organic alkali, tetramethylammonium hydroxide (TMAH). About 50-100  $\mu\text{g}$  of powdered

resin sample is mixed with 1-2  $\mu\text{l}$  of 25 wt% TMAH solution in methanol, and then introduced into the heated center of the pyrolyzer at 300-400°C. The ester linkages in the resin sample are selectively decomposed into methyl esters and ethers, and the products are separated by a capillary separation column and detected by a flame ionization detector or a mass detector.

Compositional Analysis of Multicomponent UV-Cured Resins<sup>1</sup>

Table 1 shows the typical products from acrylic esters in the UV-cured resins obtained by reactive pyrolysis in the presence of TMAH. These products were formed through reactive pyrolysis, and methylation occurred at ester linkages in the UV-cured resins. In the pyrograms of multicomponent UV-cured acrylic resins, specific products such as methyl acrylate (MA) and various methyl ethers reflecting the structures of the acrylic esters were clearly observed. The compositions of the UV-cured resins containing multicomponent acrylic esters determined based on the relative yields of the characteristic pyrolysis products of each acrylic ester showed good agreement with theoretical values estimated from the feed composition.

Evaluation of Molecular Weights of Original Epoxy Acrylate Prepolymers in UV-Cured Resins<sup>2</sup>

Original molecular weight of bisphenol-A type epoxy acrylate (BEA) prepolymer in UV-cured resins was estimated by Py-GC in the presence of TMAH. In the pyrogram of UV-cured monomeric BEA, various methyl ethers containing a bisphenol-A unit (M) were observed along with MA and some products from 2-hydroxypropyl moieties. Meanwhile, in the pyrogram of UV-cured oligomeric BEA, methyl ethers containing two bisphenol-A

## FIGURE 3

## Schematic diagram of reactive pyrolysis-gas chromatographic system using tetramethylammonium hydroxide

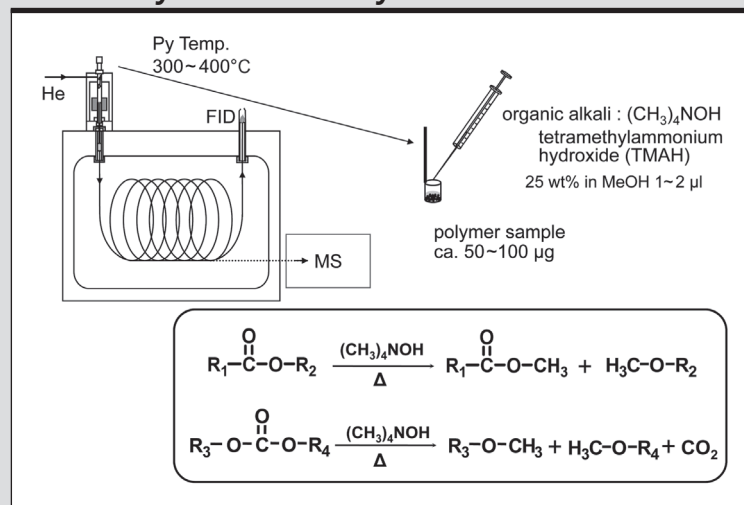
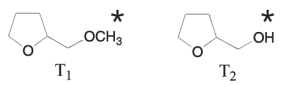
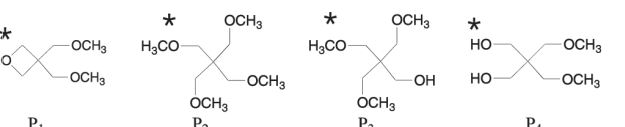
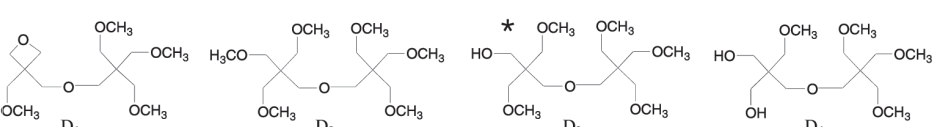


TABLE 1

## Reactive pyrolysis products from acrylic esters in the UV-cured resins

Acrylic esters moieties in the resins	Characteristic pyrolysis products from the resins <sup>a</sup>
HEA	$\text{H}_3\text{CO}-\text{CH}_2-\text{OCH}_3$ <sup>*</sup> $\text{H}_1$ $\text{HO}-\text{CH}_2-\text{OCH}_3$ <sup>*</sup> $\text{H}_2$
THFA	 $\text{T}_1$ $\text{T}_2$
NPGDA	$\text{H}_3\text{CO}-\text{H}_2\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{OCH}_3$ <sup>*</sup> $\text{N}_1$ $\text{HO}-\text{H}_2\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{OCH}_3$ <sup>*</sup> $\text{N}_2$ $\text{HO}-\text{H}_2\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{OH}$ <sup>*</sup> $\text{N}_3$
EBADA	$\text{H}_3\text{CO}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_n-\text{OCH}_3$ <sup>*</sup> $\text{E}_0 (m+n=0), \text{E}_1 (m+n=1), \text{E}_2 (m+n=2), \text{E}_3 (m+n=3), \text{E}_4 (m+n=4), \text{E}_5 (m+n=5)$
PETA	 $\text{P}_1$ $\text{P}_2$ $\text{P}_3$ $\text{P}_4$
DPEHA	 $\text{D}_1$ $\text{D}_2$ $\text{D}_3$ $\text{D}_4$

units (D) were also produced. Figure 4 illustrates the possible formation pathway of these characteristic products from UV-cured epoxy acrylate resins by reactive pyrolysis in the presence of TMAH. The relative yields of those methyl ethers containing one or two bisphenol-A units considerably varied depending on the molecular weights of the original BEA prepolymers. On the basis of relative peak intensities among the specific pyrolysis products, the average molecular weight of the BEA prepolymers in the multicomponent UV-cured resins was estimated.

### Determination of Conversion of UV-Cured Resin<sup>3</sup>

Double-bond conversion of UV-cured resins prepared from pentaerythritol triacrylate (PETA) was determined by Py-GC in the

presence of TMAH. The pyrogram of the uncured prepolymer compound contained specific products reflecting the original acrylate structure such as methyl acrylate (MA) and methyl ethers of pentaerythritol. Meanwhile, in the pyrograms of the UV-cured PETA, the yields of MA considerably decreased. The double-bond conversions of the cured resins irradiated with various UV dosages were calculated based on the relative yields of MA among the specific products in the pyrograms. The conversions determined by this approach were almost comparable with those estimated by Fourier transform infrared spectroscopy.

### Characterization of Network Structure in UV-Cured Resins<sup>4</sup>

The network structures in the UV-cured resin prepared from

poly(ethylene glycol) diacrylate (PEDA) were characterized by Py-GC in the presence of TMAH. As shown in Figure 5 (in the pyrogram of the UV-cured PEDA), various MA oligomers reflecting network structure were clearly observed along with a series of dimethyl ethers of poly(ethylene glycol) oligomers. The observed peak intensities of the MA oligomers were interpreted in terms of the chain distribution of network junctions in the UV-cured resin. The sequences observed by this method, however, were rather shorter than those expected, probably due to the inherent limitation of the GC technique.

### Characterization by MALDI-MS Combined with Supercritical Methanolysis

UV-cured acrylic ester resin samples were characterized by

MALDI-MS combined with supercritical methanolysis of the resin samples to analyze the longer sequences of network junctions.<sup>5</sup> As shown in Figure 6, the resin samples

sealed in a stainless steel tube with methanol were decomposed under supercritical conditions (e.g., 300°C, 20 MPa) to form a series of the methyl acrylate oligomers similar to the

case of pyrolysis in the presence of TMAH, followed by the MALDI-MS measurements of the methanolysis products reflecting the longer sequences of network junction.

**FIGURE 4**

**Possible formation pathway of reactive pyrolysis products from UV-cured epoxy acrylate resins**

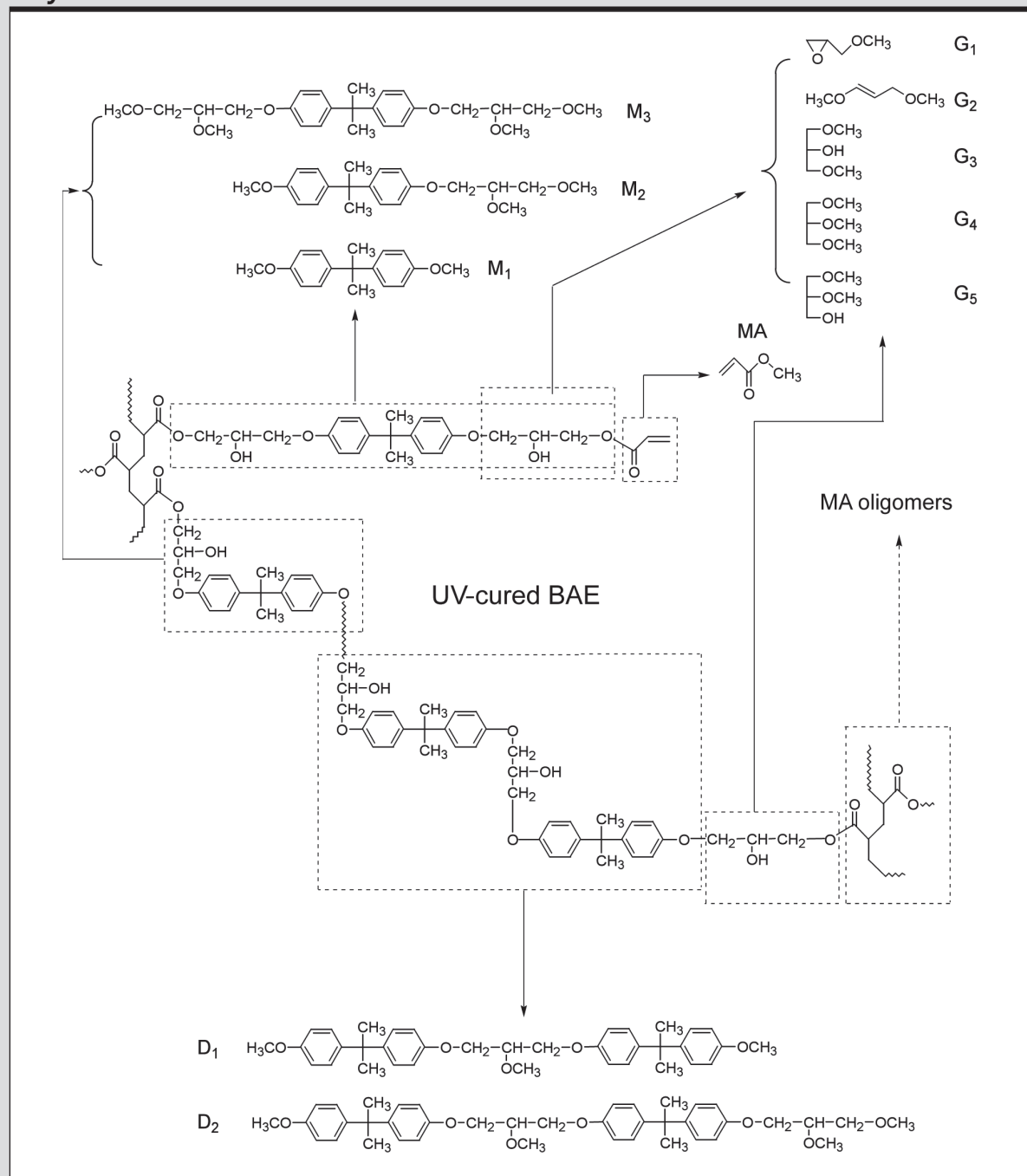


FIGURE 5

Partial pyrogram of UV-cured polyethylene glycol diacrylate observed in the presence of TMAH at 400°C and possible formation pathways of specific products of UV-cured resins by reactive pyrolysis

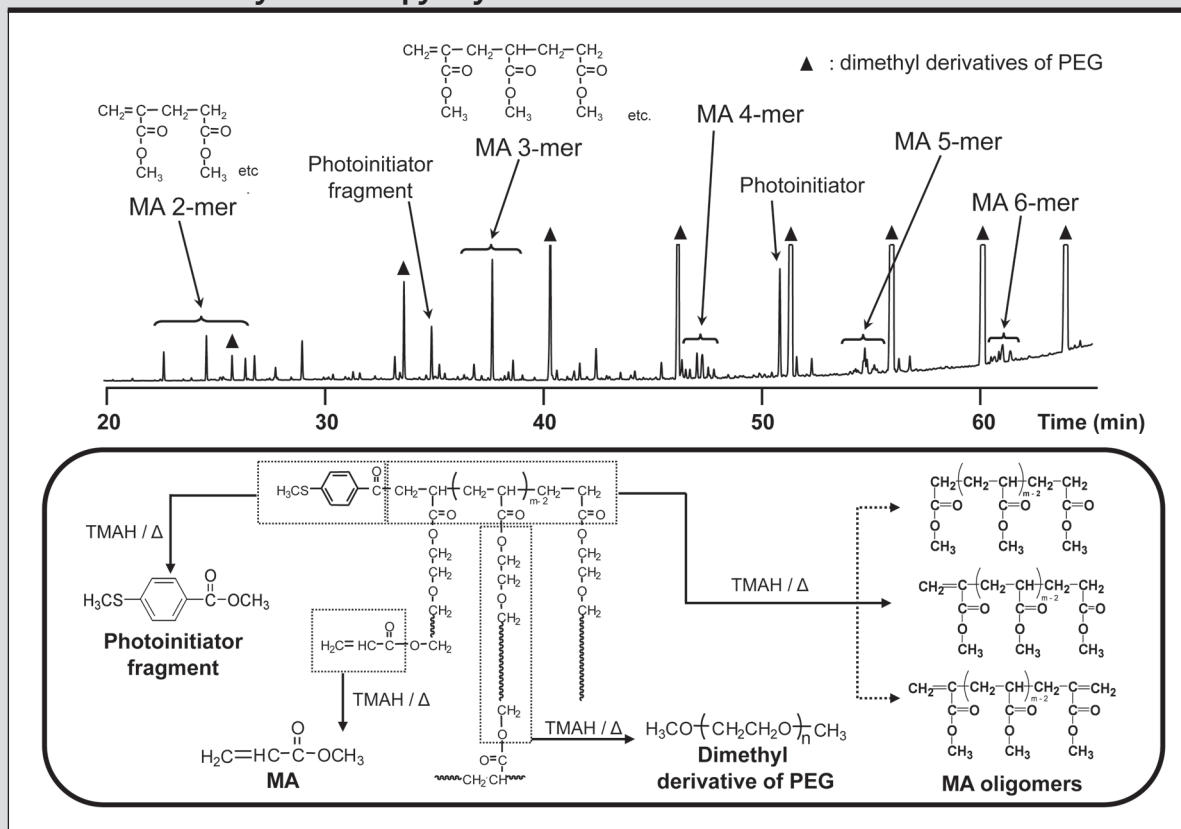


Figure 7 shows a typical MALDI mass spectrum of the methanolysis products. A series of peaks with the interval of  $m/z$  86, corresponding to the molecular weight of methyl acrylate, were observed in the  $m/z$  range up to around 4,000. This fact demonstrated that relatively longer sequences of network junctions (at least 50 acrylate units) were present in the given UV-cured system. Moreover, as shown in Figure 8, the signals of much higher molecular weight poly(methyl acrylate) (up to around 150,000 mass units) were observed in the MALDI mass spectra of the fractionated products by size exclusion chromatography. This result suggests

FIGURE 6

Apparatus for supercritical methanolysis of cured resin samples

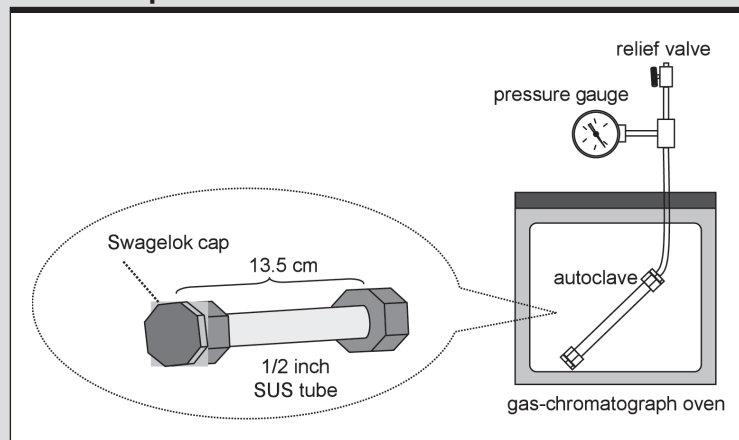
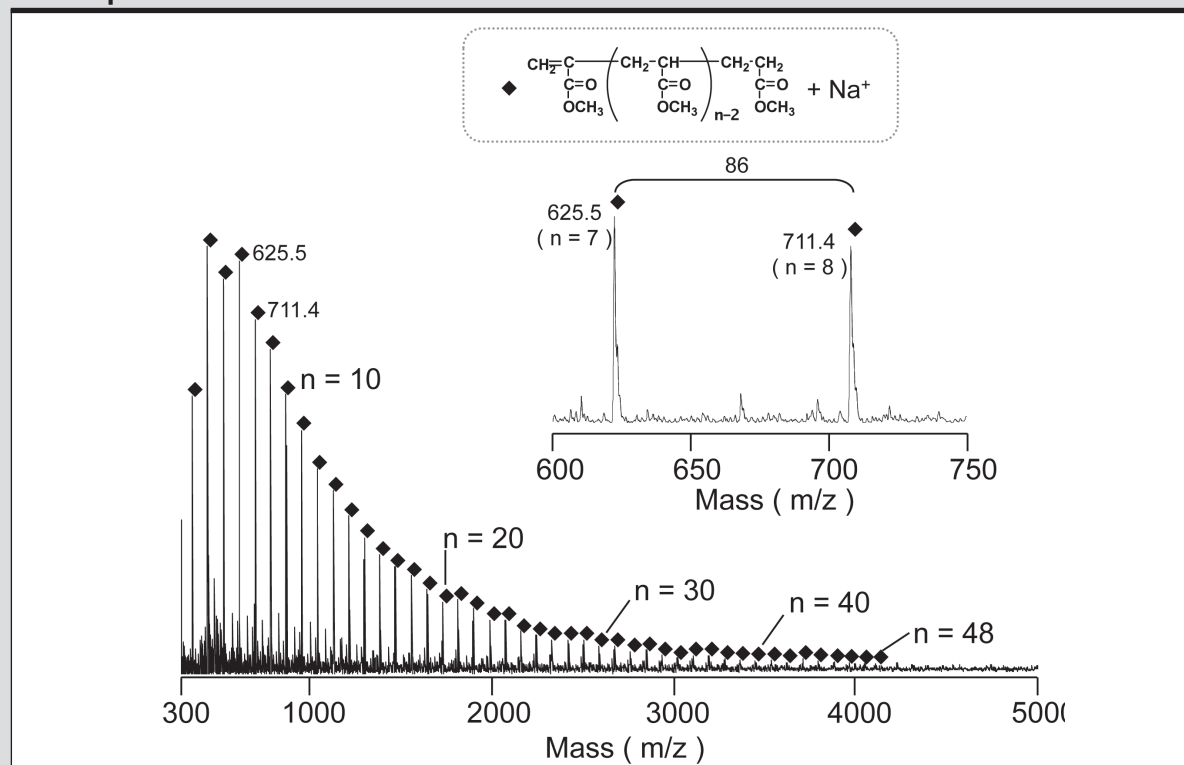


FIGURE 7

### MALDI-mass spectrum of supercritical methanolysis products of UV-cured DPHA decomposed at 290°C and 21 MPa for four hours



that the corresponding sequences of network junctions might be formed during the photocuring.

This technique was then applied to UV- and electron beam (EB)-cured acrylic resins copolymerized with vinyl pyrrolidone (VP)<sup>6</sup>. A series of the MA/VP copolymers were observed in the MALDI mass spectra of the methanolysis products of the cured resins. This fact verified the copolymerization reactions during the curing processes.

#### Conclusion

UV-cured acrylic ester resin samples were first analyzed by Py-GC in the presence of organic alkali, tetramethylammonium hydroxide. A series of products—not only those of the constituent monomers

and prepolymers, but also methyl acrylate (MA) and its oligomers (up to hexamers) reflecting the crosslinking sequences which were formed through thermally assisted hydrolysis and methylation selectively occurred at ester linkages in the cured resins—were observed in the pyrograms. These products were interpreted in terms of the chemical composition and molecular weight of the constituent monomers (prepolymers); their double-bond conversion in curing; and the sequence distributions of network junctions. Moreover, the UV-cured resins were also characterized by MALDI-MS combined with supercritical methanolysis of the samples. The methanolysis products were fractionated by size exclusion chromatography followed by the

MALDI-MS measurements of the individual fractions. The observed distributions of the decomposition products, a series of poly(methyl acrylate)s, suggested that the network junctions in the UV-cured resin were composed of up to around 2,000 acrylate units. The proposed methods would be useful to characterize rigidly crosslinked network structures in photocured acrylic ester resins widely utilized in practical applications. ■

#### References

1. H. Matsubara, A. Yoshida, H. Ohtani, and S. Tsuge, "Compositional Analysis of UV-Cured Acrylic Ester Resins by Pyrolysis-Gas Chromatography in the Presence of Organic Alkali," *J. Anal. Appl. Pyrolysis*, 64, 159-175, 2002.
2. H. Matsubara and H. Ohtani, "Evaluation of Molecular Weight

of Original Epoxy Acrylates in UV-Cured Resins by Pyrolysis-Gas Chromatography in the Presence of Organic Alkali," *J. Anal. Appl. Pyrolysis*, 75, 226-235, 2006.

3. H. Matsubara and H. Ohtani, "Rapid and Sensitive Determination of the Conversion of UV-Cured Acrylic Ester Resins by Pyrolysis-Gas Chromatography in the Presence of Organic Alkali," *Anal. Sci.*, 23, 513-516, 2007.
4. H. Matsubara, A. Yoshida, Y. Kondo, S. Tsuge, and H. Ohtani, "Characterization of Network Structures in UV-Cured Acrylic Ester Resins by Pyrolysis-Gas Chromatography in the Presence of Organic Alkali," *Macromolecules*, 36, 4750-4755, 2003.
5. H. Matsubara, S. Hata, Y. Kondo, Y. Ishida, H. Takigawa, and H. Ohtani, "Characterization of Crosslinking Structures in UV-Cured Acrylic Ester Resins by MALDI-MS Combined with Supercritical Methanolysis," *Anal. Sci.*, 22, 1403-1407, 2006.
6. H. Matsubara, H. Kataoka, and H. Ohtani, "Characterization of Network Structure in Radiation-Cured Resins of Polyfunctional Acrylic Ester and N-vinylpyrrolidone by MALDI-MS Combined with Supercritical Methanolysis," *Polym. Chem.*, 1, 1056-1061, 2010.

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## FIGURE 8

**SEC/MALDI-MS measurement of supercritical methanolysis products of UV-cured DPFA—(a) SEC curve of methanolysis products; mass spectra of (b) fraction F1 (19.5 min), (c) fraction F2 (17.5 min), (d) fraction F3 (15.5 min) and (e) fraction F4 (13.5 min)**

