Characterization of Cross-linking Structures in UV-cured Acrylic Ester Resin by MALDI-MS Combined with Supercritical Methanolysis

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The cross-linking structure of the ultra violet (UV)-cured resin prepared from dipentaerithritol hexaacrylate (DPHA) was characterized by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) combined with supercritical methanolysis. The MALDI-mass spectrum of the decomposition products obtained by supercritical methanolysis contained a series of peaks of sodium-cationized methyl acrylate (MA) oligomers up to around $m/z = 4000$ formed through selective cleavage and methylation occurred at ester linkages in UV-cured DPHA. Furthermore, in order to observe widely distributed sequence lengths in the cross-linking junctions, the decomposed products of the cured resin were then fractionated using size exclusion chromatography followed by the MALDI-MS measurements of the individual fractions. The MALDI-mass spectra of the lower molar mass fractions mainly consisted of a series of peaks of MA oligomers around m/z values of several thousands, whereas those of higher molecular weight showed a broad peak up to m/z ca. 180000. The observed distributions of the supercritical methanolysis products suggested that the network junctions in the given UV-cured resin were composed of up to around 2000 acrylate units.

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Introduction

Ultraviolet (UV) curable acrylic esters are applied to many industrial products such as printing inks, coatings for optical fibers and disks, adhesives, dental materials, photoresist, and three-dimensional stereolithography.¹⁻⁵ In order to utilize these in advanced technology, it is often requested to elucidate the cross-linking network structure of the resulting cured resins by UV-irradiation. However, it is not an easy task to analyze cured resins even using advanced spectroscopic methods mainly because of their insoluble nature. Recently, the authors characterized the chain length distribution of network junctions in UV-cured poly(ethylene glycol) diacrylate (PEDA) using pyrolysis-gas chromatography in the presence of tetramethylammonium hydroxide.⁶ In this case, methyl acrylate (MA) oligomers formed through thermally assisted hydrolysis and methylation selectively occurred at ester linkages in UV-cured PEDA were attributed to the sequences of the network junctions in the cross-linking structure. The chain length distribution of the network junctions composed of up to six acryloyl units in the UV-cured PEDA was estimated from the peak intensities of the corresponding MA oligomers observed in

the pyrogram. However, the network structure containing longer sequences comprised of more than seven acryloyl units was not elucidated because the corresponding higher MA oligomers were not observed in the pyrogram, mainly due to their lower volatility.

Meanwhile, Burkoth *et al.* evaluated the kinetic chain length of the network junctions of UV-cured dimethacrylated sebacic anhydride through matrix-assisted laser desorption/ionization-mass spectrometric (MALDI-MS) measurements of its decomposition products.⁷ This polymer was readily hydrolyzed in phosphate buffered saline at pH 7.4 and 37°C during several hours into sebacic acid and poly(methacrylic acid). They observed that poly(methacrylic acid)s reflected the sequences of network junctions in the range between pentamer and 24-mer in the MALDI mass spectra. This approach, however, was limited for the loosely cross-linking polymer composed of the hydrophilic monomers and oligomers suitable for biodegradable applications. Such materials should be much easier to be hydrolyzed than practical UV-cured resins in the industrial fields with rigidly cross-linking structure essential for high chemical resistance and heat resistance.

On the other hand, supercritical fluids such as supercritical methanol have been utilized to depolymerize intractable polymers such as poly(ethylene terephthalate) (PET)⁸ and phenol resin⁹ mainly for the purpose of plastic recycling. In the former instance,⁸ PET was almost completely decomposed in

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Fig. 1 Typical formation pathway of UV-cured DPHA.

methanol in 30 min under the supercritical conditions at 300°C and various pressures over 8.1 MPa. In this case, the ester linkages cleaved to give dimethyl terephthalate and ethylene glycol, although oligomeric products such as 4-methoxycarbonyl(2-hydroxyethyl)benzoate were also produced with the yield of 40–50%. This result suggests that the supercritical methanol is a potential solvent to cause selective cleavages of ester linkages with high efficiency even in the intractable polymeric materials.

In this work, MALDI-MS combined with supercritical methanolysis was used as an analytical method to characterize network structure of the UV-cured acrylic ester resin. First, UV-cured resins prepared from dipentaerythritol hexaacrylate utilized in the industrial fields were subjected to supercritical methanolysis to achieve selective decomposition at the ester linkages. The products thus obtained were measured by MALDI-MS to observe the sequence distributions of the network junctions. Moreover, size exclusion chromatographic fractionation of the products was combined with MALDI-MS¹⁰ to evaluate appropriately the widely distributed sequences of network junctions.

Experimental

Samples

Dipentaerythritol hexaacrylate (DPHA) was obtained from Kyoeisha Chemical. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (benzyl dimethyl ketal; BDMK, Wako Pure Chemical Industries) was used without further purification. A typical formation pathway of the UV-cured DPHA using BDMK as a photoinitiator is shown in Fig. 1. By absorbing UV light, BDMK decomposes through α -splitting to give a benzoyl radical and a dimethoxybenzyl radical. The latter radical further decomposes into a methyl benzoate and a methyl radical. Each of these radicals should contribute to initiate photopolymerization although, only the initiation by a benzoyl radical was represented in Fig. 1.¹¹

The procedure for preparing UV-cured resin samples is basically the same as that described in our previous papers.^{6,12} Prepolymers were compounded by dissolving BDMK into DPHA at 70°C together with a small amount of 1,4-benzoquinone (BQ; Tokyo Kasei Kogyo) (DPHA:BDMK:BQ = 100:3:0.5 in wt.). Here, BQ was added to prevent excessive chain growth of the cross-linking sequences. Then, each

Fig. 2 Schematic diagram of degradation apparatus used in this work.

viscous prepolymer solution was poured into a laboratory dish to form a wet film with 500–600 μm thickness. UV-curing was carried out in air by passing the UV-curable prepolymer in the dish through the UV-curing equipment consisting of a conveyor, a medium-pressure mercury lamp (80 W/cm and total output 2 kW) mounted in a dichroic mirror, and an infrared cut-off filter. The dosage for preparing UV-cured DPHA was determined to be 64 mJ/cm² by a UV-integrator (EYE Graphics UVPF-36, wavelength range = 300–360 nm). Prior to supercritical methanolysis, the UV-cured resin sample was cryomilled into a fine powder by a freezer mill (Spex 6750) at liquid nitrogen temperature in order to improve the efficiency of methanolysis.

Supercritical methanolysis procedure

Figure 2 illustrates the apparatus for degradation used in this work. The autoclave was made of a stainless-steel (SUS 316) tube (1/2 inch Φ , 13.5 cm long) with the inner volume of 10 ml, of which one end was sealed with a Swagelok cap. Twenty milligrams of the ground resin sample were put into an autoclave together with 7.5 ml of methanol. Then, the autoclave was capped with a Swagelok union connected to a pressure gage to monitor the reaction pressure. The sealed autoclave was heated at around 300°C in a gas chromatograph oven. Under these conditions, methanol in the reaction tube was in a supercritical state over the critical point (513 K and 8.1 MPa).¹³ After heating for a prescribed period, the autoclave was cooled down in a water bath, the decomposed products were taken out of the autoclave and the inner wall of the tube was

Fig. 3 Formation pathway of decomposed products of UV-cured DPHA in supercritical methanol.

washed out using tetrahydrofuran. The products in methanol were mixed with the rinsing solutions and dried *in vacuo*, and then the obtained solid products were dissolved again with 0.15 ml of chloroform to be subjected to size exclusion chromatographic fractionation and/or MALDI-MS measurement.

MALDI-MS conditions

The combination of 1,8-dihydroxy-9[10H]-anthracenone (dithranol; Sigma) and sodium iodide (Wako Pure Chemical Industries) was empirically selected as the optimum combination of matrix-cationization reagent and was used without further purification. First, 20 μl of chloroform solution containing methanolysis products of the UV-cured resin was mixed with 20 μl of tetrahydrofuran solution containing 0.1 M dithranol and 0.01 M sodium iodide. Then, 2 μl of the sample/matrix mixed solution was spotted on a stainless-steel sample plate. MALDI-mass spectra were acquired using a time-of-flight mass spectrometer (AXIMA CFR Plus, Shimadzu/Kratos) equipped with a pulsed nitrogen laser ($\lambda = 337 \text{ nm}$, 3 ns pulse width) and a delayed extraction ion source. Ions generated by the laser desorption were introduced into the flight tube with an accelerating voltage of 20 kV. The delay time was set at 90 ns. All mass spectra were acquired by averaging 100 individual laser shots under the default conditions of the spectrometer for mass calibration.

Size exclusion chromatographic conditions

Size exclusion chromatographic (SEC) measurements and fractionation were carried out using a liquid chromatograph system consisting of a pump (PU-2080 Plus; JASCO), a column oven (860-CO; JASCO) and a refractive index detector (RI-2031 Plus; JASCO). Separation was performed by packed columns Shodex K-806M and K-803 (Showa Denko) connected in series. SEC instruments were operated at 40°C using chloroform as the mobile phase (1 ml/min). The values of M_n were calculated using a calibration curve generated with monodisperse polystyrene standards. To collect the fractions for MALDI-MS measurement this procedure was used: a 0.1 ml chloroform solution of the methanolysis products was injected and 0.17 ml of the eluent was taken every 10 s into a tapered polypropylene vial. After the solvent in the fraction was evaporated, the residue was mixed with 20 μl of tetrahydrofuran solution containing 0.1 M dithranol and 0.01 M sodium iodide and the mixture was subjected to MALDI-MS measurement.

Fig. 4 SEC chromatograms of the products after supercritical methanolysis: (a) 300°C, 4 h; (b) 290°C, 4 h; (c) 290°C, 5 h.

Results and Discussion

Optimization of supercritical methanolysis conditions

In the case of methanolysis of poly(ethylene terephthalate) (PET) using supercritical methanol, dimethyl terephthalate and ethylene glycol are mainly formed through *trans*-esterification.⁸ Provided that supercritical methanolysis of the UV-cured DPHA proceeds in the same manner as that of PET, selective cleavage and methylation should occur at ester linkages in the resin. Figure 3 illustrates the most probable formation pathway of the supercritical methanolysis products of the UV-cured DPHA. Methyl acrylate (MA) oligomers and/or polymers are to be formed through selective cleavage and methylation occurred at ester linkages in the UV-cured resins. Meanwhile, dipentaerythritol moiety should be converted to dipentaerythritol. Unless the pyrolytic cleavages at C-C bonds in the sequence of acryloyl groups take place, the MA oligomers and/or polymers should reflect the chain length distributions of network junctions in the cured resin.

Figure 4 shows typical SEC chromatograms of the supercritical methanolysis products of the UV-cured DPHA decomposed under different conditions. In the chromatogram of the products decomposed at 300°C for 4 h (Fig. 4a), a continuous elution profile with two broad humps was observed. Although the first peak was thought to be chiefly comprised of poly(methyl acrylate) (PMA) formed through supercritical methanolysis, the second peak with longer retention time might be secondary degradation products formed through C-C bond cleavage of PMA due to excess thermal energy. Meanwhile, in the middle chromatogram of the products formed through

Fig. 5 MALDI-mass spectrum of supercritical methanolysis products of UV-cured DPHA decomposed at 290°C and 21 MPa for 4 h.

methanolysis at 290°C for 4 h, a single broad peak eluting from *ca.* 13 min was mostly observed, indicating that undesirable pyrolytic cleavage was minimized. Moreover, it was confirmed that methyl methacrylate monomer subjected to these conditions did not polymerize, suggesting that polymerization of the decomposition products did not take place during supercritical methanolysis. However, a longer reaction time even at the same temperature caused a small decrease in the highest molecular weight of the products, probably due to the partial contribution of pyrolytic degradation observed in the bottom chromatogram eluting from about 13 min, although the apparent average M_w values for (c) were slightly higher than those for (b). Consequently, supercritical methanolysis at 290°C for 4 h was selected as the optimum reaction condition for this work.

Characterization of network structure in the UV-cured resin

Figure 5 shows a MALDI-mass spectrum of the supercritical methanolysis products of the UV-cured resin obtained under the optimized conditions (290°C, 21 MPa for 4 h). In the mass spectrum, a series of peaks with the intervals of $m/z = 86$ were observed in the mass range up to *ca.* 4000. The intervals of $m/z = 86$ are equal to a methyl acrylate monomer and the observed m/z values of the peaks correspond to those of sodium-cationized PMA molecules having one vinylidene terminal as shown in Fig. 5. Accordingly, the network junctions in the UV-cured resin were considered to be mostly decomposed into corresponding PMA in supercritical methanol under the optimized conditions.

However, the molar mass distribution of the PMA products in the mass spectrum in Fig. 5 was somewhat shorter than that estimated from the average molecular weight observed by SEC ($M_n = 3400$ in Fig. 4(b)). This phenomenon was caused by a mass discrimination effect¹⁴⁻¹⁶ due to a broad distribution of PMA, reflecting a wide range of sequence lengths in the network junctions. In order to observe the whole range of PMA clipped out of the network junctions, therefore, the methanolysis products were first fractionated using SEC, and then the obtained fractions were subjected to MALDI-MS measurements.

Figure 6 shows the SEC chromatogram of methanolysis products of UV-cured DPHA together with the typical MALDI-

Fig. 6 SEC/MALDI-MS measurement of supercritical methanolysis products of UV-cured DPHA; (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).

mass spectra of the fractions taken at different retention times. In the mass spectrum of the fraction collected at 19.5 min (Fig. 6b), a series of peaks corresponding to the MA oligomers were mainly observed with the intervals of 86 mass units in the m/z range between 1000 and 3000. Similarly, a number of peaks corresponding to PMA in the mass range up to *ca.* 6000 were clearly obtained in the mass spectrum of the fraction at 17.5 min (Fig. 6c). In addition, although the *S/N* ratio was very low, a broad and non-resolved peak was observed in the mass spectra of the fractions having higher molecular weight (Figs. 6d and e). The edge of the peak at m/z *ca.* 180000 in the mass spectrum of the fraction at 13.5 min (Fig. 6e) might be assigned to PMA with almost 2100 repeat units. Thus, these results demonstrated that the network junctions in the given UV-cured resin were composed of rather long polyacrylate sequences ranging up to about 2000 units in length.

In conclusion, MALDI-MS combined with supercritical methanolysis made it possible to characterize the cross-linking sequences of the UV-cured resin comprised of multi-functional acrylates. Collecting SEC fractions followed by MALDI-MS analysis could evaluate almost the whole range of molecular-weight distribution of the polydispersed MA oligomers and polymers formed through supercritical methanolysis. This method would be useful to characterize rigidly cross-linked network structures in UV-cured acrylic ester resins widely used in practical applications.

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