Analysis of Minor Ingredients in Multi-functional Acrylates and their Influence on the Properties

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ABSTRACT

Recent progressive analytical equipments, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) and supercritical fluid chromatography (SFC), were applied to analyze the minor ingredients such as impurities and by-products included in commercially manufactured multi-functional acrylates (MFAs). Employing MALDI-TOF MS analysis for commercial polypropyleneglycol diacrylate (PPGDA), not only a series of homologues of diacrylate and monoacrylate with various degrees of propylene oxide (PO) repeating unit but also trace amount of glycol as a raw material could be detected due to the highly analytical resolution. Utilizing SFC technique for pentaerithritol triacrylate (PETA) analysis, several kinds of Michael addition products, which CO_2H group of acrylic acid or OH group of intermediates were reacted with double bonds of acryloyl moiety of main components, could be separated and detected.

Commercial MFAs were purified by conventional column chromatography technique for comparison between commercial and purified materials. The increase of melting point and decrease of viscosity were observed clearly in purified MFAs as expected. The refractive index of purified MFAs was slightly decreased. The significant differences of UV curability were not confirmed although the concentration of functional group of each MFA was not exactly same and further investigation was essential for rigorously kinetic comparison. By micro hardness tester analysis, it was confirmed that the surface hardness of UV cured film formed by purified MFAs was superior to corresponding commercial MFAs.

INTRODUCTION

Radiation-curing (RC) technology has achieved uninterrupted growth for the past three decades

and is expected to continue to increase in the future.[1,2] The major factors propelling gains by RC technology include the removal of solvents, the elimination of the need for heating, high production speed and excellent properties of the cured product. Acrylates has been mainly utilized in RC field as raw materials and recently epoxides and oxetanes for cationic photo-polymerizable system have started to be used widely.[3,4] New photo-initiator free systems such as maleimides[5,6] and vinyl acrylate[7] have been developed eagerly to avoid the toxicity from the fragments of photo initiators.

Generally, acrylates are produced commercially through esterification reaction of corresponding alcohol and acrylic acid. Almost all the acrylates are supplied without further purification due to the relatively higher boiling point for commercial distillation although a small part of low molecular-weight monoacrylates are supplied after distillation for purification. Therefore impurities or by-products might get mixed with the product. However there are few reports concerning minor ingredients such as impurities and by-products included in commercially available MFAs. In this work, recent progressive equipments such as matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) and supercritical fluid chromatography (SFC) were applied to analyze the minor ingredients of MFAs. Moreover comparison of properties and performance between commercial and purified MFAs was conducted and the influences caused by minor ingredients were investigated.

EXPERIMENTAL

MATERIALS

Commercially manufactured multifunctional acrylates were obtained from Toagosei Co., Ltd. The purification of commercially manufactured MFAs was conducted using conventional silica gel column chromatography with various ratios of hexane and ethyl acetate as a solvent. The chemical structures and purities of separated fractions were confirmed by ^{1}H-NMR. Their purities were more than 95%. The tested samples of commercial MFAs were used without any purification. The tested coatings for photo-DSC and hardness tester were prepared with 99 wt % of MFA and 1 wt % of 2-hydroxy-2-methyl-1-phenyl-propane-one.

METHODS AND EQUIPMENTS

LC-MS, MALDI-TOF-MS AND SFC ANALYSIS,

Liquid chromatography mass spectrometry (LC-MS), matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) and supercritical fluid chromatography (SFC) technique were utilized according to reported procedures.[8-11]

PREPARATION OF UV CURED FILMS FOR MICRO HARDNESS TESTER

The coatings of 10 um were coated on steel plates and irradiated by using high pressure

mercury lamp with the intensity of 250 mW/cm^2 under ambient atmosphere. UV dose was adjusted around 1.5 J/cm^2 at UV-A region in order to obtain the fully cured film of MFAs.

PHOTO-DSC MEASUREMENT

Heat of polymerization during photo-cationic polymerizations was measured by Differential Scanning Calorimeter (DSC220C: Seiko Instruments Inc.) equipped with UV-1 lighting unit (200W Hg-Xe lamp, Seiko Instruments Inc.). Around 2 mg of samples were applied to aluminum pan and irradiated UV light under ambient atmosphere at 25^{o}C. The light intensity was adjusted to 2 mW/cm^2 at 365nm using ND filter.

MICRO HARDNESS TESTER

The coated steel plate was submitted to the micro hardness test using Fischerscope H-100 equipped with Vickers indenter at a load 20 mN. Maximum indentation depth and permanent flaw were measured under and after load, respectively. Universal hardness was calculated from the load and maximum contact area and elastic recovery was from the maximum indentation and permanent flaw after load. [12]

RESULTS AND DISCUSSION

PRODUCTION OF COMMERCIAL ACRYLATES

Generally, acrylates are produced commercially by esterification reaction of corresponding alcohol and acrylic acid with strong acid catalyst in organic solvent. After the reaction, catalyst and excess raw materials are removed by the extraction of phase separation treatment using organic and watery phase, and then the solvent is removed under reduce pressure. Almost all the acrylates are supplied without the further purification due to the relatively higher boiling point for commercial distillation although a small part of low molecular-weight monoacrylates such as tetrahydrofurfuryl acrylate and isobornyl acrylate are supplied after distillation. Therefore impurities or by-products might be contaminated with the commercial product to a certain extent.

APPLICATION OF RECENT PROGRESSIVE EQUIPMENTS FOR COMMERCIAL MFA ANALYSIS

LC-MS ANALYSIS

Liquid chromatography mass spectrometry (LC-MS) is very widely and commonly used for compositional analysis of organic chemical compounds although high-resolution analysis of trace constituents in the range of oligomers is often difficult by LC, mainly because of its insufficient resolution. Figure 1 shows the LC spectra of commercial tetraethyleneglycol diacrylate (TEGDA). A very wide series of peaks with equal distance for corresponding homologues with various degrees of

ethylene oxide (EO) repeating unit could be detected. From the result of mass spectra, the peaks at 1.6 and 1.8 minutes could be assigned to 4 and 5 of repeating EO unit, respectively. The other ingredients like an impurity could not be observed at all.

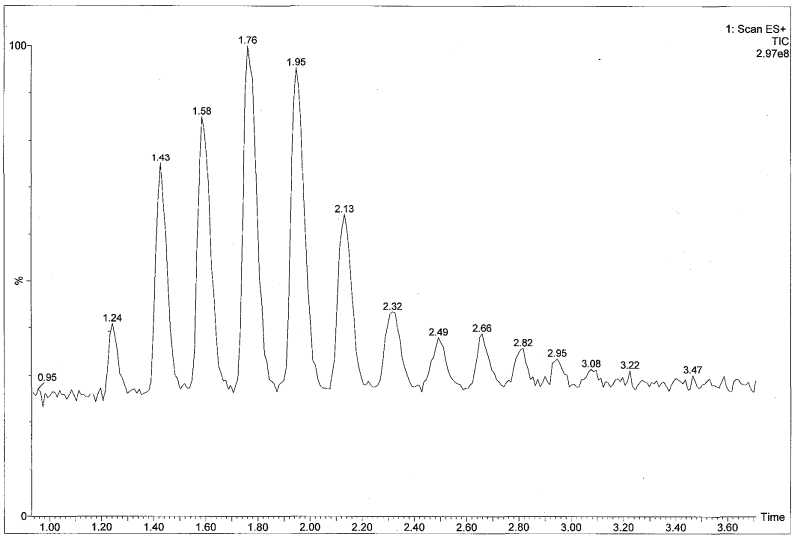


Figure 1. LC-MS spectra for commercially manufactured tetraethyleneglycol diacrylate (TEGDA)

MALDI-TOF-MS ANALYSIS

MALDI-TOF-MS was developed approximately at the same time in the later half of 1980's by Tanaka and Karas and has been recognized as a powerful method which simply yields molecular ions without any fragmentation even for oligomeric organic compounds although it is generally difficult to make quantitative analysis.

Figure 2 shows the MALDI-TOF-MS spectra of commercial PPGDA (average number of repeating PO unit is 7). Diacrylates (D_n) and monoacrylates (M_n) were observed as their Na adduct ions from 4 to 12 region. Propyleneglycol (G_n) from 6 to 9 was also detected to substantial extent. These spectra suggested that PPGDA consisted of diacrylate with considerable amounts of monoacrylates and trace amounts of PG which are mostly observed in the low molecular-weight region. [9,10]

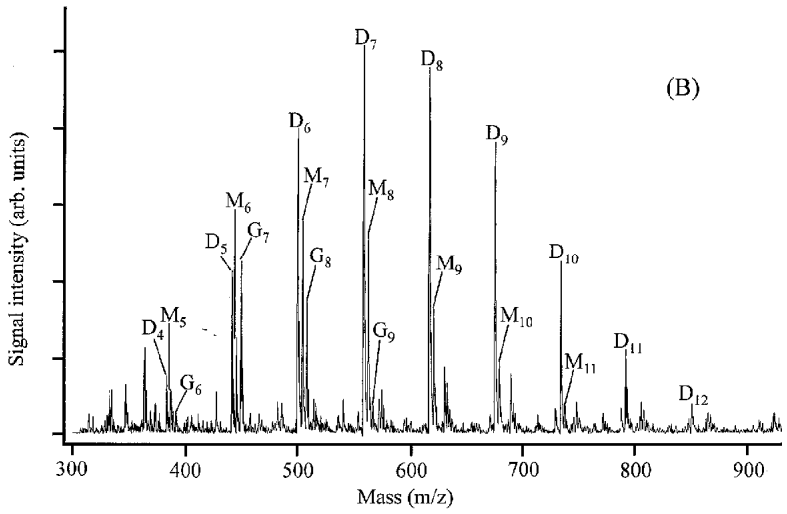


Figure 2. MALDI-TOF-MS spectra of commercial polypropylenegrycol diacrylate (PPGDA)

SFC ANALISYS

Supercritical fluid chromatography (SFC) was reported in 1962 by Klesper for the first time and the basic technology was established in middle of 1980's. SFC is often suitable to separate the oligomeric mixtures with a wide range of boiling points, which compensates for drawbacks of gas chromatography (GC) and LC. So far, SFC has been applied to the separation of various polymer homologues in the oligomer region.

Figure 3 shows the SFC chromatograms of pentaerythritol triacrylate (PETA) using CO_2 as a mobile phase in temperature programming and modifier gradient mode for better separation. The main components (peaks1-3) confirmed by the ^{1}H NMR spectra of the corresponding fraction. These proved to be PETA homologues containing tetra-, tri-, and diacryloyl groups, respectively, which eluted in the order of their polarities. The minor components (peak c-e) were estimated to be the adducts between one acrylic acid and three kinds of main components like type A in scheme 1 by ^{1}H-NHR. Similarly the peaks f-h were the adducts between main components and formed by self-addition like type B in scheme 1. [11]

Employing recent progressive equipments, MALDI-TOF-MS and SFC, the minor ingredients such as raw material and Michael adducts included in commercial MFAs could be detected and assigned successfully.

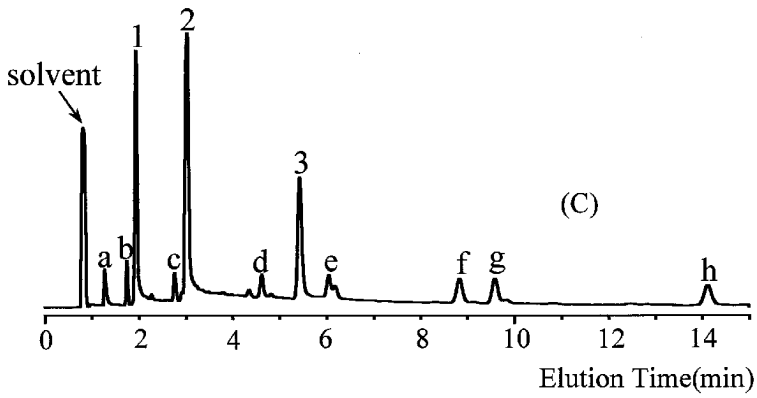
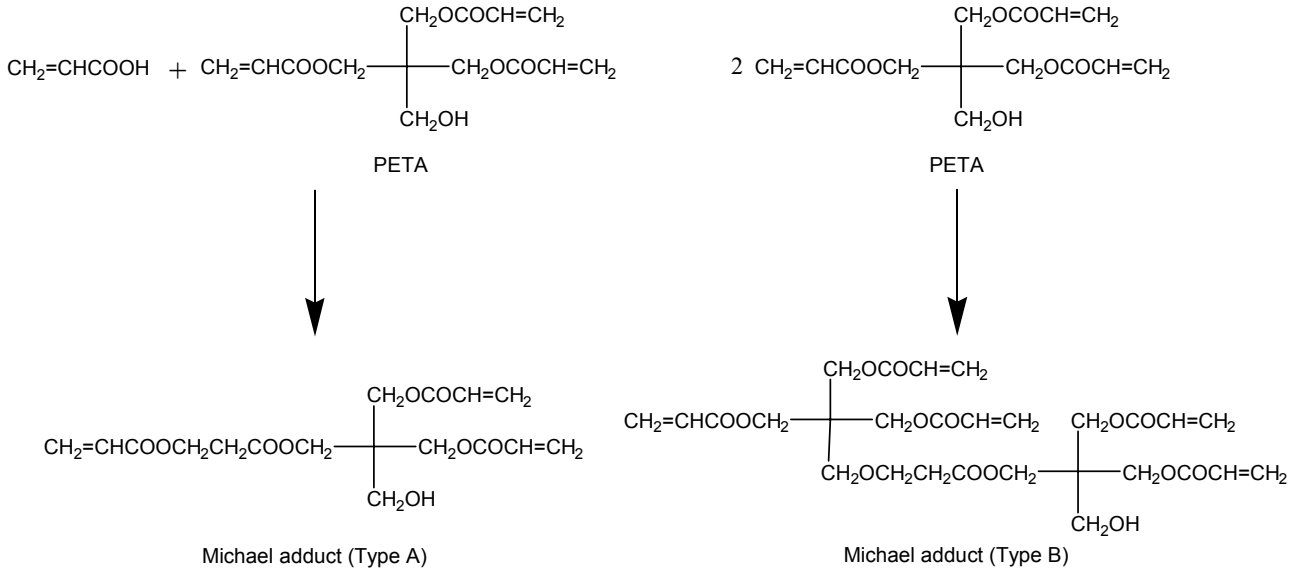


Figure 3. SFC chromatogram of pentaerythritol triacrylate (PETA)



Scheme 1 Typical possible formation mechanism of Michael addition products of PETA

COMPARISON OF PROPERTIES AND PERFORMANCES BETWEEN COMMERCIAL AND PURIFIED MULTI FUNCTIONAL ACRYLATES

CHEMICAL PROPERTIES

Commercial MFAs were purified by conventional column chromatography technique for comparison between commercial and purified materials. Table 1 shows the chemical properties of commercial and purified MFAs. The increase of melting point and decrease of viscosity were seen clearly in purified MFAs as expected by purification. The refractive index of purified MFAs was slightly decreased.

Table 1. Chemical properties of commercial and purified MFAs

		Appearance	Melting Point °C	Viscosity mPa·s/25°C	Specific gravity D/25°C
DPHA	Commercial	Viscous liquid	-	6,100	1.489
	Purified	Crystal	59	-	-
DPPA	Commercial	Viscous liquid	-	8,400	1.490
	Purified	Viscous liquid	-	2,900	1.488
PETETRA	Commercial	Wax	43-50	-	-
	Purified	Crystal	54	-	-
PETA	Commercial	Liquid	-	600	1.485
	Purified	Liquid	-	360	1.484

UV CURABILITY

UV curability was compared between commercially manufactured MFAs and purified ones with photo-DSC. Figure 4 and 5 show the results of photo-DSC for pentaerythritol triacrylate (PETA) and dipentaerythritol pentaacrylate (DPPA), respectively. In case of PETA, UV curability of purified formulation seemed to be superior to commercial one. But in case of DPPA, commercial material was slightly better than purified. Commercial MFA contains Michael adducts to some degree, which brings the decrease of concentration of functional group. Contrarily, commercial PETA contains di- and tetra-acrylate and similarly DPPA might contain tetra- and hexa-acrylate, which means the uncertainty of concentration of functional group.

Therefore, the significant differences of UV curability were not confirmed in this study although the concentration of functional group of each MFA was not exactly the same and further investigation was essential for rigorously kinetic study.

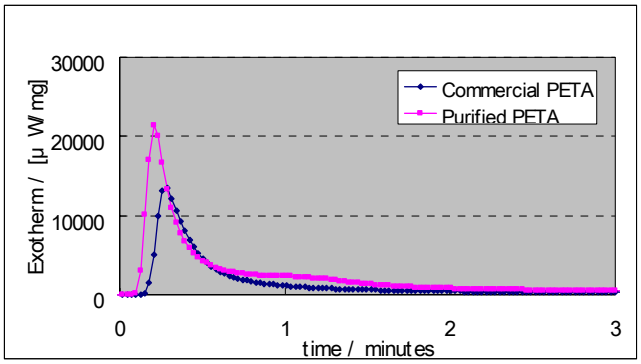


Figure 4. Photo DSC for commercial and purified PETA

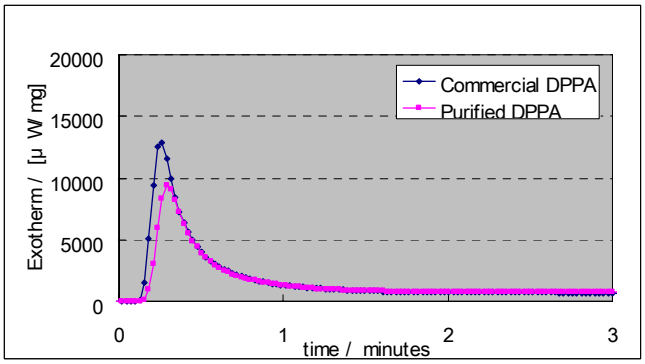


Figure 5. Photo DSC for commercial and purified DPPA

HARDNESS OF UV CURED FILMS

Dipentaerythritol penta-acrylate (DPPA), hexa-acrylate (DPHA) and pentaerythritol tri-acrylate (PETA), tetra-acrylate (PETETRA) are widely used for RC formulations such as UV hard coatings, inks and photo resists due to highly crosslinkable acryloyl functionality. Therefore the hardness of cured film is one of the most considerable properties for MFAs. The results of hardness of MFAs after UV curing are summarized in table 2. The hardness for commercial and purified DPHA shows 368 N/mm^2 and 412 N/mm^2, respectively. Similarly PETETRA gives 394 N/mm^2 and 422 N/mm^2. The hardness was enhanced by purification in all MFAs used in this work. Clear correlation was confirmed in the concentration of functional group and hardness after UV curing. Elastic recovery also has close relation to abrasion resistance on the surface.[12] The elastic recoveries of all MFAs were increased by purification, which expects purified materials might give the better abrasion resistance coatings.

Table 2. Universal hardness and elastic recovery measured by micro hardness tester

		Universal Hardness N/mm^2	Elastic recovery %
DPHA	Commercial	368	78
	Purified	412	83
DPPA	Commercial	344	75
	Purified	384	81
PETETRA	Commercial	394	78
	Purified	422	80
PETA	Commercial	367	66
	Purified	371	69

CONCLUSIONS

Recent progressive analytical equipments, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) and supercritical fluid chromatography (SFC), were applied to analyze the minor ingredients such as impurities and by-products included in commercially manufactured multi-functional acrylates (MFAs). Employing MALDI-TOF MS analysis for commercial polypropyleneglycol diacrylate (PPGDA), not only a series of homologues of diacrylate and monoacrylate with various degrees of propylene oxide (PO) repeating unit but also trace amount of glycol as a raw material could be detected due to the highly analytical resolution. Utilizing SFC technique for pentaerithritol triacrylate (PETA) analysis, several kinds of Michael addition products, which CO_2H group of acrylic acid or OH group of intermediates were reacted with double bonds of acryloyl moiety of main components, could be separated and detected.

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