The Effects of UV Energy Density and Peak Irradiance on the Non-Crosslinked Components in UV-Polymerized Films

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ABSTRACT

A size exclusion chromatography (SEC) investigation was conducted to determine the types and relative amounts of non-polymerized and/or non-crosslinked components of ultraviolet (UV)-polymerized films. This study initially involved the use of a 2^4-factorial experimental design to optimize the flow rate, temperature, sensitivity, and injection volume for the SEC instrumentation. These optimized parameters, along with optimized solvent extraction techniques, were then used to determine the effects of UV energy density and peak irradiance on the type and level of solvent-extractable components in the polymer films. Since solvent-extractable components are *not* chemically bound into the three-dimensional crosslinked polymer network that forms during photopolymerization, the ability to experimentally determine the amount and composition of such components may be useful for explaining several effects of UV energy on the kinetics of the UV polymerization process. Such data may also be beneficial in commercial applications where the quantity of solvent-extractable material must be minimized.

INTRODUCTION

Ultraviolet (UV) polymerization and crosslinking is a "curing" process that is used in many industrial applications. These applications normally require materials that form a crosslinked polymer network to achieve the desired physical and chemical properties for a particular application. Even though such polymer films are crosslinked, there are always components within them that are not chemically bonded into the three-dimensional polymer network following UV polymerization. These "fugitive" components contribute, both negatively and positively, to the overall properties of the polymer. It is of interest to determine what these components are in a given system, what their concentrations are in the polymer film, and ideally, what their presence in the film indicates about the UV energy density (also known as "UV dose") and peak irradiance effects on the kinetics of polymerization and the resulting polymer morphology.

Since these components are not chemically bonded to the crosslinked polymer, they can often be readily extracted from the film by solvent extraction techniques. The crosslinked polymer network itself is, of course, *not* soluble, since to "dissolve" it would require the breaking of covalent chemical bonds. This would "decompose" the crosslinked polymer rather than "dissolve" it. Therefore, only the non-crosslinked components, whether they be monomers, oligomers, linear or branched polymers, photoinitiators, or other formulation additives, can, in principle, be extracted with an appropriate solvent. By carrying out such extractions, information about the total concentration of the extractable components as well as the identity of those components can be ascertained when appropriate standards are used[1].

Through the use of size-exclusion chromatography (SEC) – also known as gel permeation chromatography (GPC) – these solutions of extracted material can be processed to separate, identify, and quantify the "fugitive" components in the film. SEC involves the use of a high performance liquid chromatography (HPLC) system with an integrated SEC column. Together, these are used to separate components of differing molecular size. Since molecular size is often proportional to molecular mass, this technique provides a relative measure of the molecular masses of the extractable polymer film components.

This separation method uses a packed column wherein the packing contains molecular-sized voids of varying sizes. When the components dissolved in a solvent are introduced into the column, the similar sized components begin to aggregate. The larger components pass through the column very easily and, in the resulting chromatogram, always appear first. The smaller size components are more easily trapped in the voids of the column and, thus, take more time to pass through the column. An example separating two solvent-soluble components from each other by SEC techniques is shown in **Figure 1**.

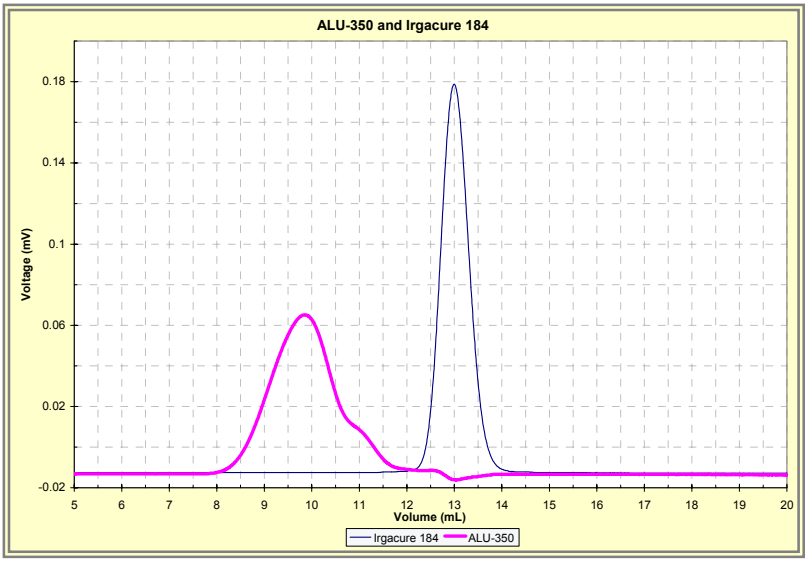

Figure 1
SEC separation of Acrylated Aliphatic Urethane Oligomer and Photoinitiator

This figure shows the difference in elution volumes (proportional to elution time) between two key solvent-soluble components of a UV-polymerizable formulation. These two components, the oligomer and the photoinitiator, differ markedly in molecular size and, therefore, elute from the SEC column at different times. The heavier and larger oligomer molecules elute first (peak on the left) and then the much smaller photoinitiator molecules exit the column later. The SEC technique, then, allows for relative molecular masses and amounts of the various components of the mixture to be determined. These relative values for a given sample can be ascertained by integrating the area under each curve for molecular mass and measuring the relative peak heights for the relative amount of each component.

In a previous study, laboratory techniques for extraction, separation, identification, and quantification of non-polymerized or non-crosslinked components were optimized. The optimization of these conditions involved a numerical 2^4-factorial designed experiment, the

results of which were presented during the Poster Session at RadTech 2002 in Indianapolis[1]. Once these optimum conditions were determined, it was then possible to use these parameters to accurately determine the effects of UV energy density and peak irradiance on the solvent extractables of UV-polymerized films using SEC methodology.

Most linear and branched polymers have the ability to be dissolved and, therefore, a relative molecular mass average for a sample can be determined using SEC techniques. When combined with laser light scattering technology, absolute weight average molecular masses (M_w) can be determined. However, the polymers that are produced by photopolymerization processes are almost always crosslinked, three-dimensional polymeric networks. To dissolve such substances would require the breaking of covalent bonds. Thus, these polymers are insoluble by definition and their molecular masses cannot be determined through conventional methods. In fact, relatively speaking, their molecular masses can be thought of as "infinite", since the entire crosslinked film can be thought of as being a "single giant molecule". So for a 10.0-gram sample of crosslinked film, the "molecular mass" in "grams per mole" would be 6.02×10^{24} g/mol! Only 1.00 mole of these 10.0-gram "molecules" would have a combined mass of 0.100 % that of the entire earth, which is 5.98×10^{27} g [2]. Most would agree that this is essentially "infinite" molecular mass!

Since there is no direct method for determining the average molecular mass of a crosslinked polymer film, nor is there any rationale, given their "infinite" molecular masses, for trying to make such a determination, the only other option for applying SEC technology to crosslinked polymer systems is to analyze those components within the polymer that do dissolve; those components that, for whatever reason, are not chemically connected into the crosslinked polymer network. These components can be extracted from the polymer film with appropriate solvents and are, thus, known as "extractables". By determining properties of these extractables such as composition, molecular mass, and relative abundance, some generalizations can be made about the photopolymer itself and about the process by which it was formed. Thus, the purpose of this investigation was to use solvent-extraction and SEC techniques to determine the effects of UV energy density and peak irradiance on the nature and quantity of extractables obtained from UV-polymerized films.

EXPERIMENTAL

Materials

ALU-350, a polyether-based acrylated aliphatic urethane oligomer, was provided by Echo Resins and Laboratory and was used without further purification.

Isobornyl acrylate (IBOA), 1,6-hexanediol diacrylate (HDODA), and trimethylolpropane triacrylate (TMPTA) were all provided by Surface Specialties UCB and were used without further purification.

Irgacure®184, a Norrish I cleavage-type photoinitiator, 1-hydroxycyclohexylphenyl ketone, was provided by Ciba Specialty Chemicals Corporation and was used without further purification.

HPLC-grade ethyl acetate was obtained from Sigma-Aldrich Chemical Company. It was sonicated and filtered before use.

Glassware

Model number B7950 glass vials were obtained from National Scientific and used as extraction vessels. They were rinsed with 5 milliliters of HPLC grade ethyl acetate (two per extraction sample) prior to use.

Other common laboratory glassware included the following: A 400-mL beaker, a 10-mL graduated cylinder, a 125-mL flask with side arm and rubber connections, a fritted glass filter – one per film sample, a filter adapter, a rubber connection, and a 1-hole stopper.

Laboratory Equipment

Common laboratory equipment used in the extraction process included steel spatulas, a heated sonicator, a desiccator, and plastic covers made of Mylar® polyester film. These covers had many holes punched in them and were attached to the fritted glass filters to prevent polymer film samples from "flying out" of the filter during the handling and drying.

Instrumentation

A Fusion UV Systems, model F600 UV curing unit with a 600 W/in H-Bulb and model DRS 120 movable web was provided by Fusion UV Systems, Inc.

An Electronic Instrumentation and Technology (EIT) UV PowerMap™ was used to determine the UV-A energy density and peak irradiance used in the polymerization process.

A Waters 515 HPLC Pump with an injector was used in conjunction with a Wyatt Technologies miniDAWN and Optilab DSP for the collection of data. An integrated computer using ASTRA chromatography software was used to collect and analyze the data, which was then exported to Microsoft® Excel. An HR-1 Styragel® packed column was used as the SEC column.

A 60°C model # FS-14 constant temperature sonicator from Fisher Scientific was used to improve the efficiency of the extraction process. The polymer film samples were immersed in the solvent and the mixture was then sonicated for three hours before filtering to separate the extractable solution from the polymer films.

Procedures

Polymer films were made using a 65/35 mass ratio of an oligomer/monomer mixture consisting of the acrylated aliphatic polyether-based urethane oligomer and a 1:1:1 mass ratio of the three acrylate-functional monomers. The photoinitiator was post-added to the formulation at a level of 2.0 pph based on the total mass of the other components. This formulation was then applied in a thin liquid film to a sheet of Mylar®polyester film. The coating was covered with another layer of polyester to help minimize oxygen inhibition during polymerization and to aid in the process of preparing a film of relatively uniform film thickness. More details of the techniques used to prepare the formulation and to make the polymer films have been reported previously by Christmas and Matranga[3].

Attempts were made to make films at the same UV energy density at each peak irradiance value. However, some small variation in this parameter was inevitable. **Table 1** shows the UV-A energy density and peak irradiance values obtained, along with the average of each set of UV energies. For the extraction studies, two polymer films were prepared from the model formulation at each different UV energy and peak irradiance value listed.

TABLE 1
UV-A Energy Density and Peak Irradiance Values

Peak Irradiance mW/cm^2	UV Energy 1 mJ/cm^2	UV Energy 2 mJ/cm^2	UV Energy 3 mJ/cm^2	UV Energy 4 mJ/cm^2	UV Energy 5 mJ/cm^2
Notch 1: 2270	824	605	--	--	122
Notch 2: 1833	792	595	394	191	117
Notch 3: 1303	863	626	411	197	110
Notch 4: 913	821	607	394	197	98
Notch 5: 754	830	614	412	199	104
Notch 6: 614	808	615	410	201	96
Notch 7: 516	808	613	409	205	98
Notch 8: 459	816	617	408	197	99
UV Energy Mean	**820**	**612**	**405**	**198**	**106**

***Sample Preparation* -**

The outer portions of the polymerized films along with the Mylar film cover were trimmed off with scissors. The remaining film was then peeled from the Mylar base sheet and cut into squares of approximately 0.5 cm^2. These samples, called “chips” or “film chips”, can be stored for extended time periods in an airtight container away from external sources of UV light, if necessary.

***Extraction Procedure* -**

Since two films were made for a single UV energy density, approximately 0.5 g of chips from each of the two films was placed into the same 50-mL vial equipped with a Teflon® septum. Then 20.0 mL of HPLC grade ethyl acetate were added to the vial. Shaking the closed vial for 15 seconds allowed the film chips to separate and the ethyl acetate to flow freely over the film. The films were allowed to settle into the ethyl acetate and then the vial with the mixture of film chips and solvent was placed into a preheated 60°C sonicator. In a previous study[1] three hours in the sonicator was determined to be an optimum time for complete extraction on non-crosslinked components. Keeping the films in the solvent for extended time (up to three months) was found to have had no effect on the amount or type of extractables[4].

After sonication, the solvent-immersed films were filtered through the fritted filter using an aspirator vacuum. Four washings of 5-mL aliquots of HPLC grade ethyl acetate were used to aid in the removal of extractables from the film chips. Once all 20 mL of ethyl acetate were added, a circle of Mylar was affixed to the filter, to prevent loss of film chips. The solvent was collected for further study using SEC techniques.

The extracted film samples were left at ambient conditions for 15 minutes in a fume hood and then placed in a desiccator for three hours for drying. At the end of the three hours, a mass measurement was made. Subsequent mass measurements continued until a constant mass was obtained, indicating the complete removal of the solvent.

***SEC Procedures* -**

The HPLC system was calibrated at a temperature of 35°C. The flow rate was set on the HPLC as 0.2 mL/min and was left at that rate for 2 hours. Once the two-hour period passed, a 500-microliter sample of extractable was drawn up with a syringe. On the sample inlet, the knob was turned to load and the sample was injected into the injection port. The knob was turned to inject the sample and simultaneously, the computer program was started to begin recording the data.

RESULTS AND DISCUSSION

Sample Preparation Techniques

It was realized during the course of this investigation that though the formulations were being polymerized under a Mylar polyester cover sheet, the UV-A energy and peak irradiance measurements were being made without a cover sheet over the sensor "window" of the radiometer. Therefore, the samples were actually exposed to less UV-A energy than what was being recorded. While almost all of the work in this laboratory is directed toward relative comparisons, it seemed useful in this study to determine more accurately the actual UV energy and peak irradiance impacting the films during polymerization and crosslinking. Thus, the radiometer sensor was covered with a small piece of the same polyester film used as a cover sheet for the samples before it was passed under the UV lamp.

Having selected the UV energy density and peak irradiance values to be used in this investigation, approximately 50 different polymer films were prepared and replicated. This resulted in approximately 100 films to evaluate. Polymer films that were exposed to the solvent extraction process were approximately 0.08 mm to 0.14 mm in thickness with an average film thickness of 0.11 mm. A completely uniform film thickness is not essential, but can have some effects on the amounts of extractables. Since the amounts of extractables depend on the surface area available and the mass of the samples are approximately the same, a slightly thicker film will have a smaller surface area. The extraction process depends on a larger surface area because extractables can only be removed through the surface.

Film thickness also has an effect on the depth of cure. If a thicker film sample is used, there may be portions of the film that are not thoroughly polymerized. This could either leave un-polymerized components deep within the crosslinked polymer matrix that would not be in contact with the solvent during extraction, or it could lead to a higher quantity of extractables from the lower parts of the film not reached effectively by the UV energy. Thus, care was taken to insure that the film thickness was as uniform as possible, using a manual method of application.

Extraction Techniques

In order to analyze the non-crosslinked material in UV-polymerized films, a specific procedure was developed to allow for efficient and reproducible results from the extraction of those components. The development of these techniques began with a literature search to see what other extraction work might have been reported. An extraction process reported by Kloosterboer et. al.[3] was determined to be a good starting point and specific solvents reported in that paper were investigated. The screening of these solvents resulted in the selection of HPLC grade ethyl acetate as the solvent of choice. It was found to have good solvency for all the raw materials used in the model formulations and was used in 20-mL aliquots for each sample of film chips.

It was clear from the beginning that if the differences in the mass of extractables from films polymerized using different levels of UV energy density and peak irradiance were to be observed, the total mass of films chips from each sample used for extraction needed to be the same as that of all the other samples. Clearly, a larger sample of film chips would produce a higher total amount of extractables. Thus, sufficient numbers of film chips were prepared from each crosslinked polymer sample to have a total mass of 1.0 g.

A series of filtration and drying methods were examined during this investigation. They evolved to a more efficient process over time. Initially a 100°C oven was used to dry the film samples after filtration. However, when some films began to yellow when placed in the oven, a decision was made to eliminate high temperature drying methods. It then became necessary to find a method that was as effective at drying the samples as the oven method had been. This lead to a pair of side-by-side experiments, one involving the initial oven-drying method and the other involving the drying of the samples at room temperature in a desiccator containing calcium sulfate as the desiccant. **Table 2** shows that a change in the drying method from a 100°C oven to a room temperature desiccator does not have a large impact on the percent extractables.

TABLE 2
PERCENT EXTRACTABLES RELATED TO DRYING CONDITIONS

	Mass Before Extraction (g)	Mass After Extraction (g)	Percent Extractables
Oven Dried Films	**1.0102**	**0.9815**	**2.841%**
Dessicator Dried films	**1.0031**	**0.9750**	**2.801%**

On average five mass measurements were necessary for each sample to get to a constant-mass condition. The percent extractables were then calculated for each sample by subtracting the final mass of extracted films from the initial mass of the film samples. This result was then divided by the mass prior to extraction and multiplied by 100%. This calculation gives the percent of the materials in the initial film that were *not* chemically bonded to the crosslinked polymer network.

Size Exclusion Chromatography (SEC) Techniques

Standard Solutions

In order to determine the composition of the extractables, it was necessary to make standard solutions of all components of the formulation. A series of different concentrations of each monomer and oligomer, and the photoinitiator were made. The selected concentrations were based on the percent extractables obtained from actual film samples and the formulation composition.

The selection of the concentrations for the standard solutions was influenced by the average percent extractables at the lowest UV energy, 106 mJ/cm^2. At this UV energy density it was assumed that a higher percentage of the active material would remain unreacted. Actual extractable measurements at this UV energy level corroborated this assumption. The average percent extractables at 106 mJ/cm^2 for all levels of peak irradiance was 7.055%, as seen in **Table 3**.

Table 3
Percent Extractables at 106 mJ/cm^2

Peak Irradiance for Lowest UV Energy Films	Percent Extractables
Notch 1: 2269.5 mW/cm^2	6.501 %
Notch 2: 1833.2 mW/cm^2	6.775 %
Notch 3: 1302.7 mW/cm^2	6.944 %
Notch 4: 913.39 mW/cm^2	7.162 %
Notch 5: 754.06 mW/cm^2	7.654 %
Notch 6: 614.16 mW/cm^2	7.617 %
Notch 7: 515.53 mW/cm^2	6.723 %
Notch 8: 459.34 mW/cm^2	7.062 %
Average	**7.055 %**

From this average, the appropriate concentrations for preparing calibration curves for the standards were determined by the following method: Assuming a 100.00-gram sample of monomer and oligomer blended with 2.00 parts per hundred of photoinitiator, a 102.00-gram sample results. Of this total mass, the monomers constitute a total of 35.00 grams. Thus, each monomer individually makes up 11.67 g or 11.44% of the sample. The oligomer mass (65.00 g) would give 63.73% of the total formulation, and the photoinitiator (2.00 g) constitutes 1.96% of the total formulation.

If the average maximum extractables were then taken as a “worst case scenario” and it was assumed that the constituents extracted in direct proportion to their content in the formulation, then one would expect each monomer to constitute 0.8071% of the material extracted. The oligomer, then, would make up 4.496% of the extractables and the photoinitiator would represent 0.138 %. The sum of these percentages is, of course, 7.055%

The monomer standard solutions were made by using these percentages. The calculated concentration of each monomer is 0.8071%. To complete the extraction, however, a second

20-mL aliquot of ethyl acetate was used to "wash" the chips. The washings were added to the extractable solution. Thus, the final concentration of the solution was one-half of that of the original solution. This gave a value of 0.4036 %, which is the concentration of **Standard C**. Since at least three standards are necessary for a calibration curve, this concentration was cut in half to give the concentration for the second solution, **Standard B**. This solution was also halved to obtain the smallest concentration, **Standard A**. These concentrations for the monomer standard solutions are listed in **Table 4** long with the concentrations for all of the other standard solutions.

TABLE 4
CALCULATED CONCENTRATIONS OF FORMULATION COMPONENTS

Component	Standard A	Standard B	Standard C
IBOA, HDODA, TMPTA	0.1009%	0.2018%	0.4036%
Photoinitiator	0.0309%	0.0692%	0.1000%
Urethane Oligomer	0.2149%	0.3223%	0.4297%

The photoinitiator standards were made in the same manner. The photoinitiator represents 0.138% of the extractables. This was divided by two, but in this case, this concentration of 0.0690% was used as the middle value (**Standard B**). The lower concentration was obtained by dividing **Standard B** by 2 to give the concentration of **Standard A**. A concentration 0f 1.000% was chosen for **Standard C** because this was the standard concentration in the previous optimization study and because relatively more photoinitiator extracts from the films than do the other components that are at least partially crosslinked in to the polymer network. These are also listed in **Table 4**.

A slightly different method was used to determine the concentrations of oligomer in ethyl acetate. Since extraction of oligomer is never as high as that of the other components it is more logical to use the lowest amount of extractables when determining concentrations of the oligomer standards, rather then the highest. The lowest percent extractables were found at the highest average UV energy density utilized, 820 mJ/cm^2, as expected. The extractables at 820 mJ/cm^2 are listed in **Table 5** along with an average of the percent extractables.

Table 5
Percent Extractables at 820 mJ/cm^2

Peak Irradiance for Highest UV Energy Density Films	Percent Extractables
Notch 1: 2269.5 mW/cm^2	2.845 %
Notch 2: 1833.2 mW/cm^2	2.503 %
Notch 3: 1302.7 mW/cm^2	2.702 %
Notch 4: 913.39 mW/cm^2	2.577%
Notch 5: 754.06 mW/cm^2	2.676 %
Notch 6: 614.16 mW/cm^2	2.826 %
Notch 7: 515.53 mW/cm^2	2.643 %
Notch 8: 459.34 mW/cm^2	2.801%
Average	**2.697 %**

When using the average of the lowest percent extractables, the percentage of oligomer calculated was 1.719% of the extractables. This percentage was then divided by two to obtain the concentration of extracted oligomer after adding another equal volume of ethyl acetate for washing. Since the resulting concentration of 0.8595 % was deemed to be too high for the likely amount of oligomer to be extracted, it became necessary to reduce the concentration by another factor of 2, giving a concentration of 0.4397% for **Standard C**. The smallest concentration was found by dividing the largest concentration by 2 which gave **Standard A**, and the middle concentration was the mean of both the high and low concentrations (**Standard B**). **Table 4** lists all the calculated concentrations.

The standards were prepared by adding the mass into a tared 25 mL volumetric flask. The mass was calculated by dividing the calculated percentage of each standard by 100 to cancel out the percentage and was subsequently multiplied by the 25 mL volume of solution that would be placed into the volumetric flask.

Since there was much variation between the actual delivered masses and the calculated masses, the actual concentration was determined by dividing the added mass by 25 mL and multiplied by 100 to give the exact percentage. Standard solutions B were not very close to the calculated value. They were 0.1 percent over the calculated value. Since the mass measurements for B were all close, it was decided to use these concentrations instead of making new standards. In the case of calibration curves, as long as there are concentrations within the limits of the highest value, it was appropriate to use these actual concentrations. The actual concentrations are listed in **Table 6**.

TABLE 6
ACTUAL CONCENTRATIONS OF STANDARD SOLUTIONS

Component	Standard A	Standard B	Standard C
IBOA	0.0944 %	0.2920 %	0.4216 %
HDODA	0.1040 %	0.2868 %	0.4352 %
TMPTA	0.1176 %	0.2860 %	0.4204 %
Oligomer	0.2116 %	0.2864 %	0.3460 %
Photo-initiator	0.0344 %	0.0639 %	0.1036 %

These standard solutions were prepared in order to construct a calibration curve for the determination of extracted components. They were subjected to SEC analysis from which their elution volumes and maximum voltages (peak height) were determined. The elution volumes are inversely related to the size (molecular mass) of the components and the peak height is directly proportional to the relative amount of the component in the extractable solution.

A calibration curve consists of a plot of the three concentrations of a particular standard solution versus the voltage recorded on the y-axis of the chromatogram. If this plot is

reasonably linear, then it can be used to determine the concentration of the extractable that elutes at the same elution volume. These calibration curves are shown in Figure 8.

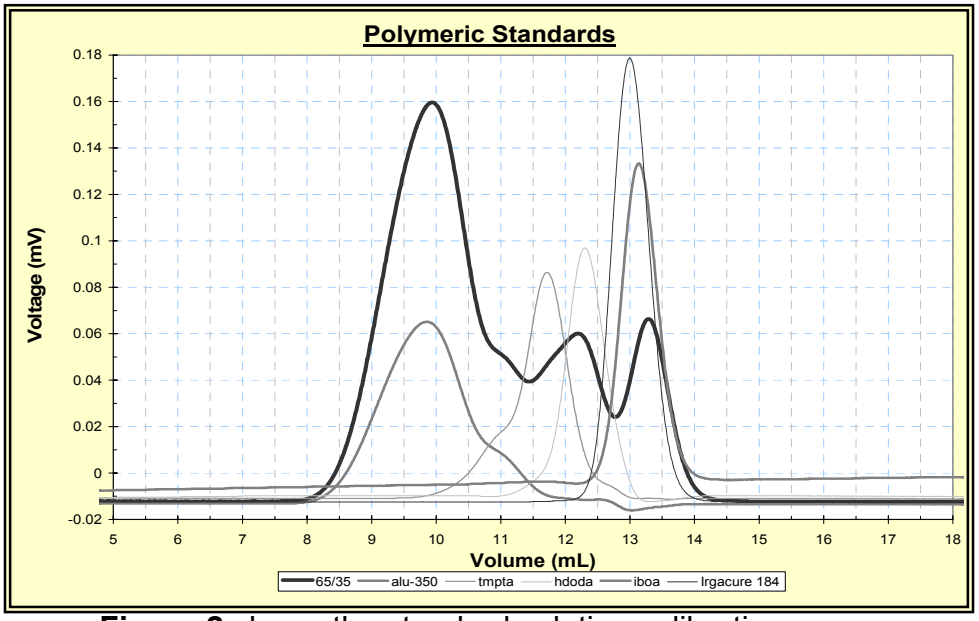

Figure 2 shows the standard solution calibration curves used in this investigation.

Using known standards allows for both qualitative and a quantitative analyses to be performed on the extractable solutions. The elution volume, maximum voltage, and peak area of each component can be determined for the extractable solutions using SEC techniques. By comparing the elution volumes of the known components in the standard solutions with those in the extractable solution, the components that have been extracted from the polymer films can be qualitatively identified. Measuring the maximum voltage (peak height) of each component along with the calibration curve allows for the determination of the relative concentration of extracted components. The peak area is helpful in determining the possible concentration of overlapping components in the chromatogram. **Figure 2** shows SEC

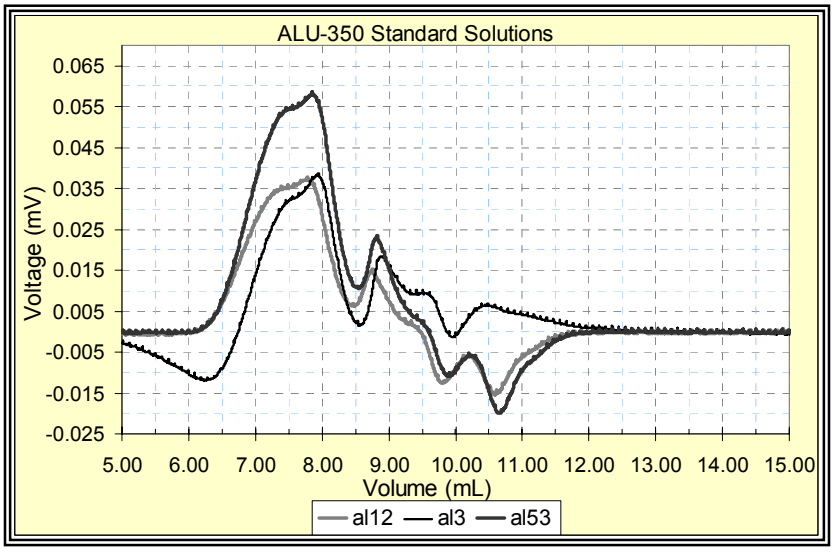

Figure 3 Alu-350 Standards

chromatograms for the standard solutions of the different components at a single concentration. The superimposed dark curve is a chromatogram of a solvent solution of the non-polymerized 65/35 formulation.

The standard solution for the oligomer had the smallest elution volume, indicating the highest molecular mass. The chromatogram for the oligomer standard solution indicates that there are several different molecular mass components present, as would be expected for most oligomers. The second chromatogram (second major peak from the left in **Figure 2**) represents the trifunctional monomer, TMPTA. It, too, has a "shoulder" on the high molecular mass side, indicating the presence of at least two components. The difunctional monomer, HDODA, eluted next and has a relatively symmetrical peak. Finally, there are two quite symmetrical peaks for the photoinitiator and the IBOA monomer respectively. These two formulation components have similar molecular masses and this is indicated by the overlap apparent between their elution curves. Such an overlap in the extractable curves can cause a problem in trying to identify the separate amounts of these two components extracted.

Interestingly, in the SEC chromatogram for the whole formulation shown in **Figure 2**, the right-most peak is probably due mainly to the IBOA since the concentration of the photoinitiator is relatively much smaller. However, for extractable solutions, the reverse would likely be true since a smaller percentage of the photoinitiator is expected to actually react compared to the percentage of reacted IBOA. This chromatogram also gives indication of significant overlap between the TMPTA peak and that of HDODA. In this particular sample, these two components were not resolved.
All of the chromatograms for the individual standards are given in F**igures 3** through **7**.

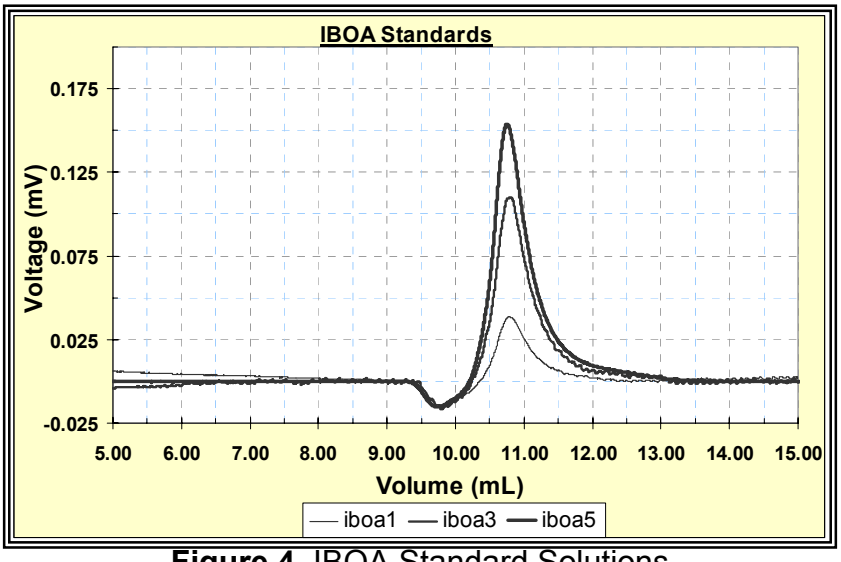

Figure 4 IBOA Standard Solutions

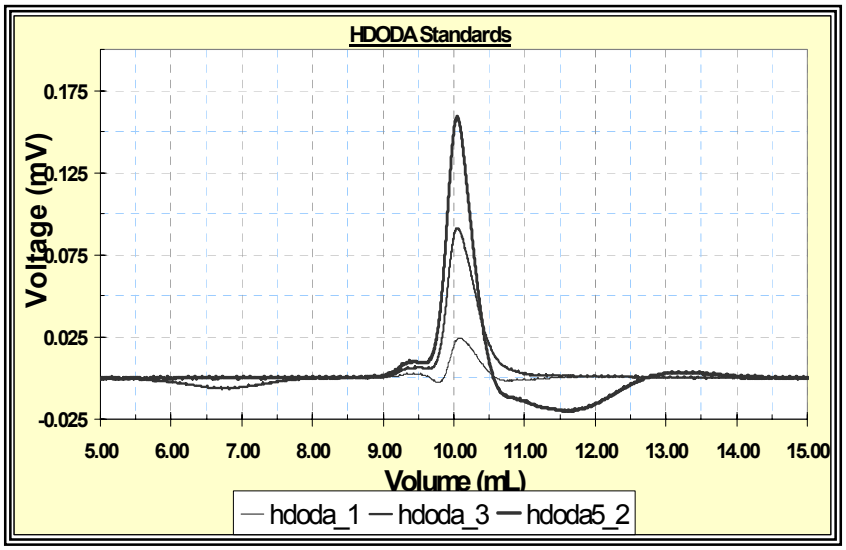

Figure 5 HDODA Standard Solutions

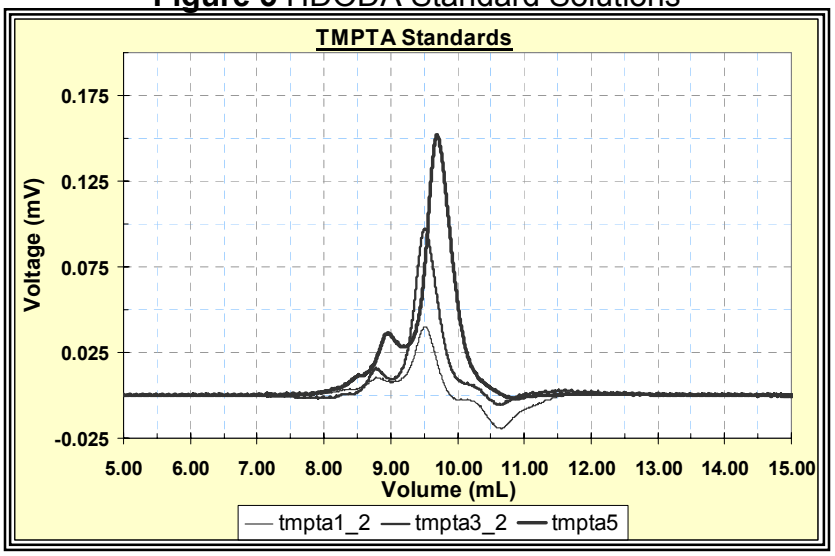

Figure 6 TMPTA Standard Solutions

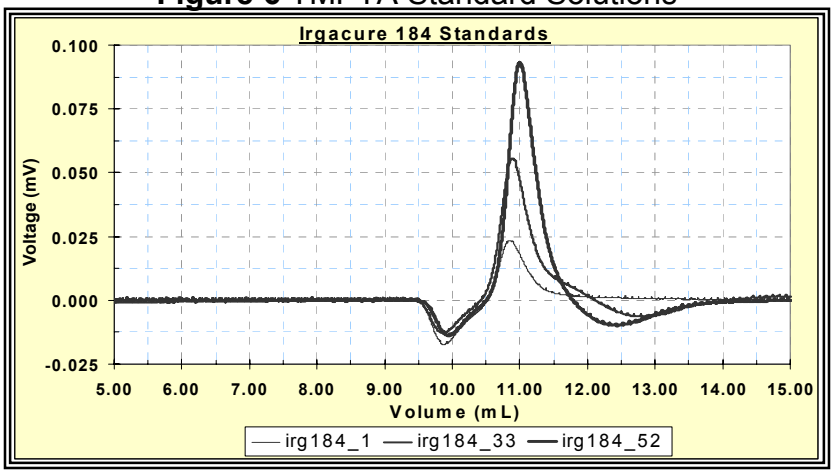

Figure 7 Irgacure® 184 Standard Solutions

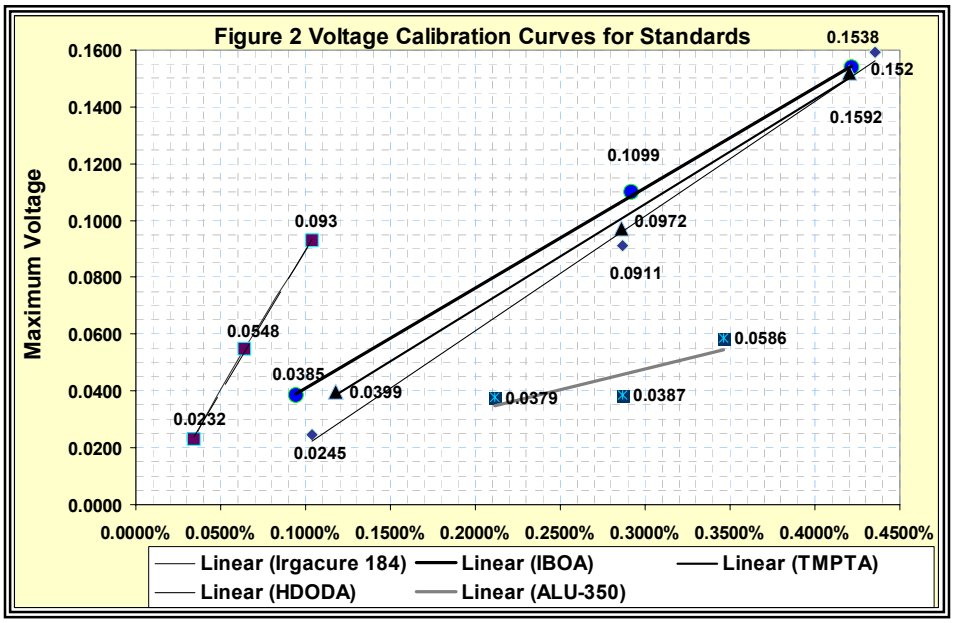

Figure 8 Calibration Curve for All Standard Solutions

SEC of Extractable Materials

With the elution volumes for each component, it was possible to detect those components using SEC. If any component had been extracted from the polymer film that did not have an elution volume similar to one of the standard chromatograms, it would suggest that some polymerization or oligomerization might have taken place. This would indicate that non-crosslinked polymers had been synthesized that, in principle, could still be extracted. No such components were identified in this study.

The SEC data given in **Figures 9** thru **13**indicate that the largest component extracted at all energy density and peak irradiances values was the photoinitiator. This was to be expected since, for practical purposes related to relative reactivity and line speed, photoinitiator levels are usually at higher levels than would be necessary if polymerization were taking place over a longer period of time. Also, only a fraction of the photoinitiator molecules absorb photons and of those that do, only a fraction actually initiate polymerization. This is related to the quantum yield of the system in question[6]. Thus, excess photoinitiator is always present in formulations of the type used in this study.

Some amount of IBOA, HDODA, and oligomer were also extracted from most samples. The trifunctional monomer, TMPTA, however, was not largely detected among the extractable materials. This was most likely due to relatively high functionality of the TMPTA. Not only does this monomer have more functionality than the other components, but also, on a molar basis, it has the lowest molar concentration of any of the monomers. Both of these factors would tend to insure that TMPTA was essentially completely polymerized into the crosslinked polymer network.

At the highest energy density and peak irradiance values, not much oligomer was extracted. However, as UV energy density decreased, the amount of oligomer in the extractables increased. This explained why the amount of percent extractables increase as energy density is decreased. This trend was seen in all peak irradiances tested. The only difference was that as the peak irradiance decreased, the amount of photoinitiator decreased and the amount of oligomer increased. This simultaneous increase and decrease of the concentration of these components allowed for the total amount of percent extractables to appear close even with differing peak irradiance. The following chromatograms show the changing concentrations of each component at changing energy densities. Note that they are different peak irradiance.

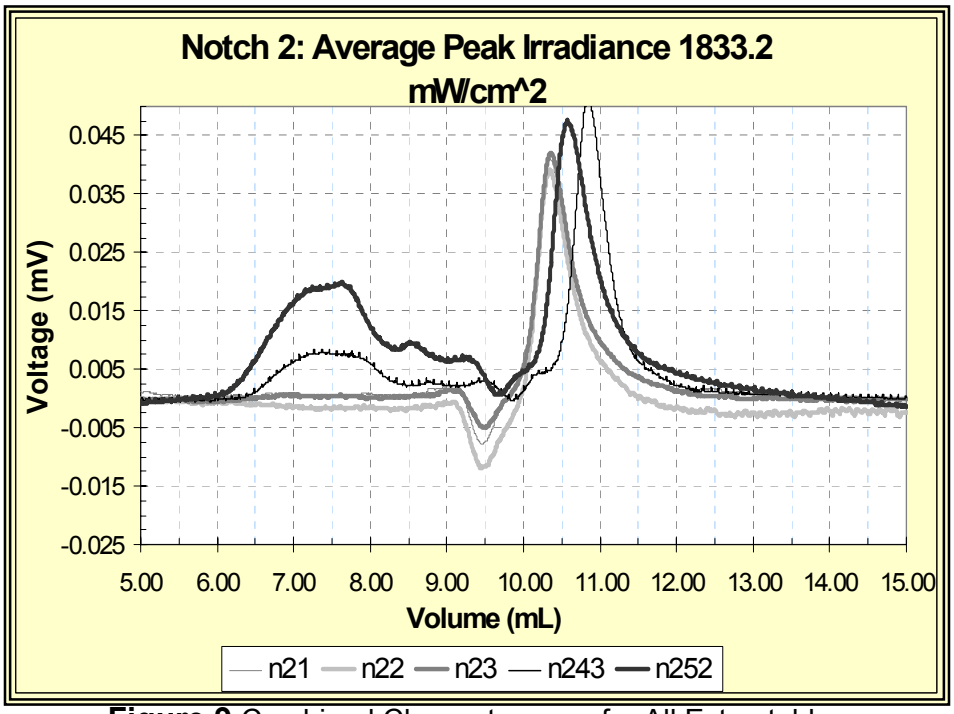

Figure 9 Combined Chromatograms for All Extractables Made at peak Irradiance 1833.2 mW/cm^2

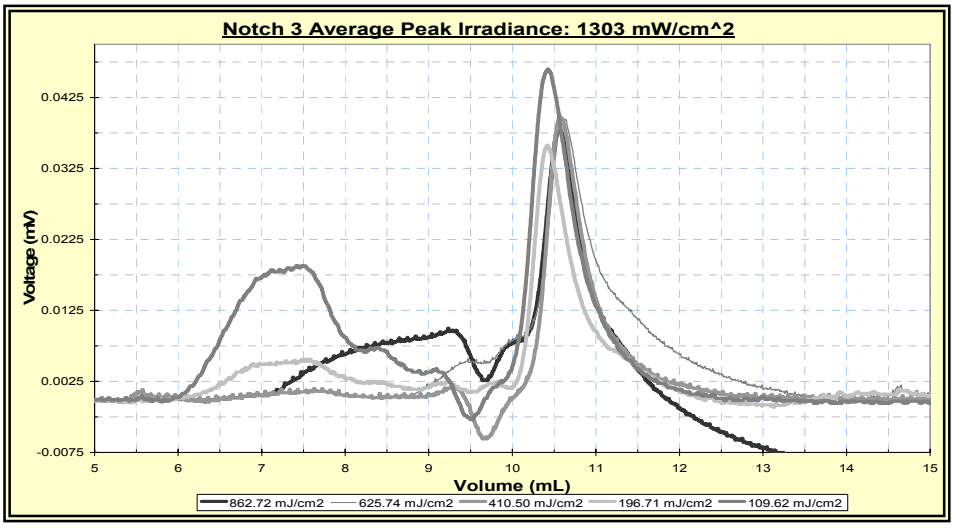

Figure 10 Combined Chromatograms for all extractables Made at Peak Irradiance 1303 mW/cm^2

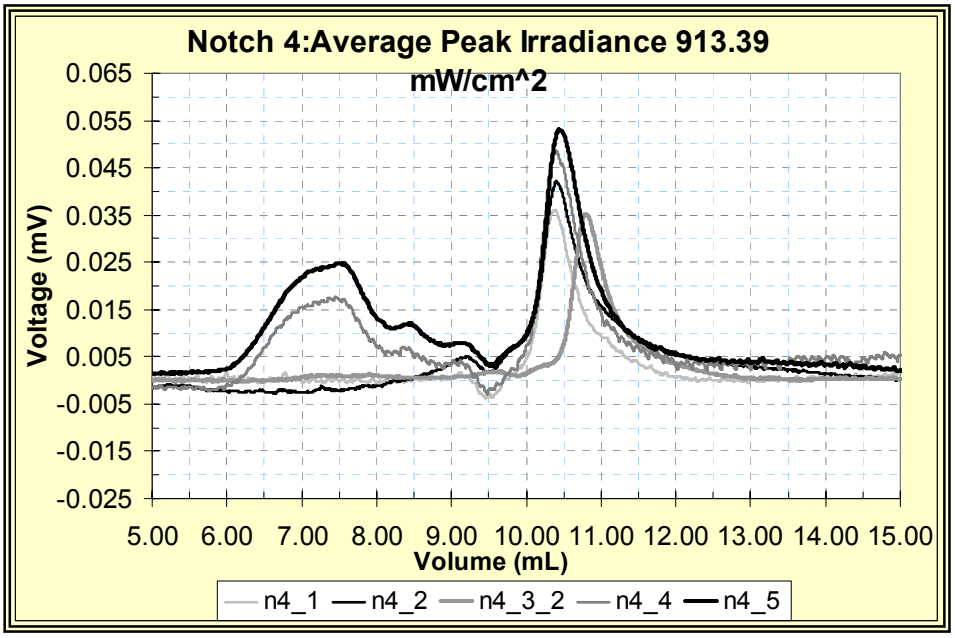

Figure 11 Combined Chromatograms for All Extractables Made at peak Irradiance 913.39 mW/cm^2

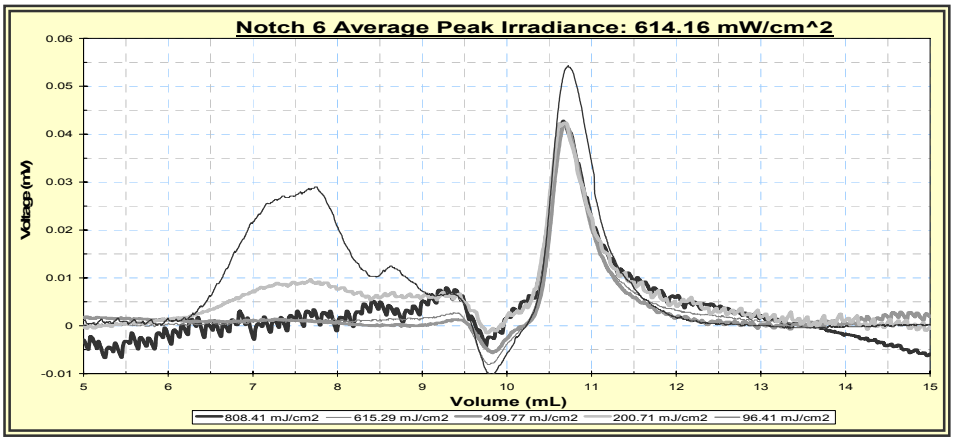

Figure 12 Combined Chromatograms for All Extractables Made at peak Irradiance 614.16 mW/cm^2

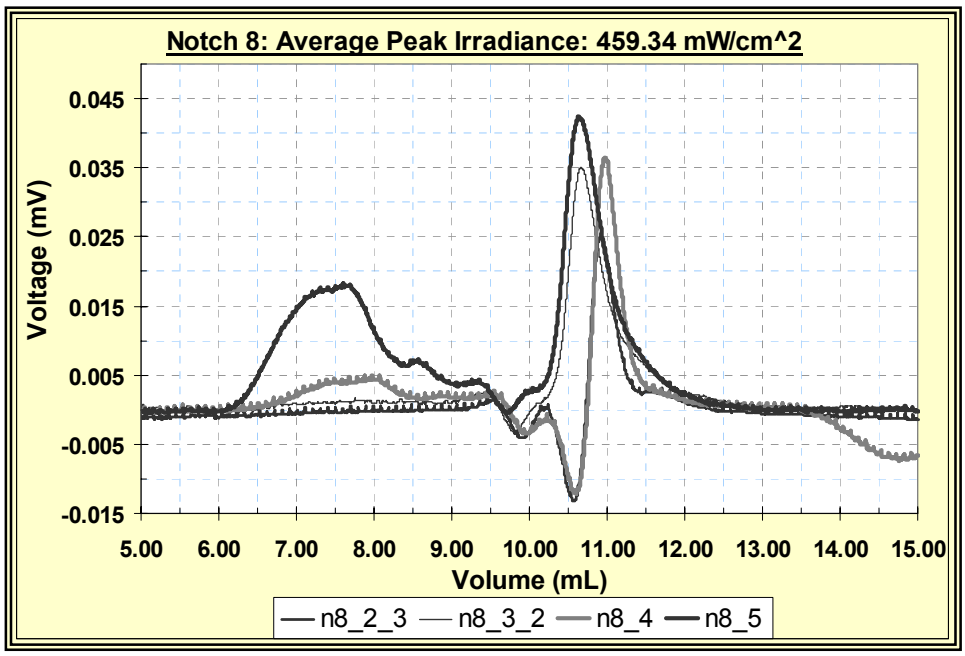

Figure 13 Combined Chromatograms for All Extractables
Made at peak Irradiance 459.34 mW/cm^2

Figures 9 through **13** are all chromatograms of extractables made at five different UV energy density values. Based on the different scale it is apparent that at lower peak irradiance, a larger percent of extractables occurs.

Table 7 lists the maximum voltages for two main peaks in all extractables. This data can be used to determine the exact percentage of each component that can be extracted out with solvent.

TABLE 7 LISTING OF MAXIMUM VOLTAGES FOR SELECTED EXTRACTABLES

	Peak 1: approximate volume 7.5 mL	Peak 2: approximate volume 10.5 mL
Notch 2		
792.00 mJ/cm^2	-0.001	0.0410
595.20 mJ/cm^2	-0.0016	0.0391
394.41 mJ/cm^2	0.0004	0.0421
190.51mJ/cm^2	0.0079	0.0511
117.45 mJ/cm^2	0.0195	0.0476
Notch 4		
820.59 mJ/cm^2	0.0004	0.0361
607.39 mJ/cm^2	-0.0018	0.0421
393.66 mJ/cm^2	0.0011	0.0352
196.64 mJ/cm^2	0.0177	0.0488
97.73 mJ/cm^2	0.0247	0.0530

Notch 6		
808.41 mJ/cm^2	0.0019	0.0395
615.29 mJ/cm^2	0.0008	0.0385
409.77 mJ/cm^2	0.0022	0.0451
200.71 mJ/cm^2	0.0081	0.0422
96.41 mJ/cm^2	0.0288	0.0526
Notch 8		
816.03 mJ/cm^2	-0.0003	0.0258
617.05 mJ/cm^2	0.0013	0.0351
408.30 mJ/cm^2	0.0049	0.0364
99.30 mJ/cm^2	0.0181	0.0425

SUMMARY AND CONCLUSIONS

Experimental methods have been developed for extracting non-polymerized and/or non-crosslinked components of UV-polymerized films, for making polymer standards, and for optimization of the use of SEC (GPC) technology to separate, identify, and quantify the extracted material. A relatively wide range of UV energy and peak irradiance values were tested in this study, but there is a need to investigate lower peak irradiance values.

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