DIELS-ALDER TRAPPING OF PHOTOCHEMICALLY GENERATED
DIENES WITH ACRYLIC ESTERS: A NOVEL APPROACH TO
PHOTOCURED POLYMER FILM DEVELOPMENT

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Introduction
Diels-Alder cycloadditions have been utilized in polymer synthesis as
an alternative to condensation reactions. 1 In our earlier efforts, we developed a
new method for the preparation of linear aromatic polyesters, which employ o-
quinodimethanes (o-QDMs), generated by a well-known photochemical
reaction: the photoisomerization of o-methylphenyl ketones. 2 Photolysis of o-
methylbenzophenone 1 produces hydroxy-o-quinodimethane 2, which can be
trapped with dienophiles, such as dimethyl acetylenedicarboxylate, 3 to efficiently
yield the corresponding cycloadduct (Scheme 1). Here we extended this
approach to a novel photocuring process for development of polymer films. We
synthesized a series of molecules with multiple o-methylphenyl ketone
functionalities. We further investigated these molecules as photoreactive
monomers to obtain polyester films through Diels-Alder cycloadditions. 4

Scheme 1

1

Experimental
Materials. All reagents were used without further purification.
Cyclohexanone (99+%), 1,6-hexanediol diacrylate, pentaerythritol
triacylate and methyl acrylate were purchased from the Aldrich Chemical Co.

Instrumentation 1H and 13C NMR spectra of the ketones were obtained on
a Bruker AC-200 spectrometer. CDCl3 containing 1% TMS as an internal
reference was used as the solvent. Irradiation studies were performed using a
Fusion UV Systems HP-6 equipped with a high-powered six-inch UV
lamp system and a VPS-3 power supply.

General Synthesis for Ketones. To a stirred solution of the
corresponding nitrile in dry tetrahydrofuran (THF) under nitrogen was added
dropwise a solution of 2-methyl phenylmagnesium bromide in THF. The
resulting mixture was refluxed under nitrogen for 18 hours. The reaction mixture
was then allowed to cool down to room temperature and poured into a saturated
aqueous solution of NH4Cl. The organic phase was collected and the aqueous
phase extracted with THF. The organic extracts were combined and dried over
Na2SO4. The solvent was dried in vacuo to yield the crude product. A (1:1)
mixture of concentrated HCl and H2O were added to that product and the
resulting mixture was refluxed for 18 hours. The mixture was then cooled down
to room temperature and extracted with CH2Cl2. The combined organic extracts
were then washed with a 5%aq. NaOH solution. The solvent was dried to yield
the crude product. Products were further purified either by recrystallization or
column chromatography. The products were characterized by 1H and 13C NMR.

General Procedure for the Film Curing by Irradiation. A solution of
the ketone, 1,6-hexanediol diacrylate diacrylate (HED), pentaerythritol
triacylate (PPT) and methyl acrylate in cyclohexanone was prepared. This
solution was transferred into a tin pan and placed in an infrared chamber. The
chamber was then purged with a stream of Argon for 5 minutes and passed under
the UV irradiation source. The UV lamp intensity was set at 65% and the belt
speed at 1. After each pass the chamber was allowed to cool down for 2 minutes.
Resulting films were further dried in a vacuum oven at 55°C for 96 hours.

Results and Discussion
To obtain polymer films with different properties, we synthesized an array of
molecules having multiple o-methylphenyl ketone sites (3-8) (Figure 1). All
ketones were synthesized from the precursor dimethylinonitrile by Grignard
synthesis with yields higher than 50%.

To obtain the linear polymer backbone growth in photocuring process, we
employed 1,6-hexanediol diacrylate (HED) 9 as a dienophile. This
molecule with the long alkyi chain contributes further molecular mobility to
the system, compensating for the loss of entropy due to high molecular weight
development. We also employed pentaerythritol triacrylate (PPT) 10 as a
dienophile to obtain increased strength by crosslinkage. Furthermore, we used
methyl acrylate 11 as an end-cap to control the molecular weights of the
polymer.

We chose cyclohexanone as the solvent for photocuring studies. Cyclohexanone,
a solvent with a high boiling point, minimizes the possibility of evaporation that
can effect the degree of polymerization by uncontrollably varying the concentrations of the solutions. Also, in our earlier studies, we demonstrated that cyclohexanone does not interfere with the desired photoen
formation step.

To obtain a systematic understanding of the effects of diketone type and
other experimental variables on the polymerization and the final polymer
properties, we chose a Design of Experiments (DOE) approach. According to
our DOE, we performed 18 film-curing experiments. Type of the diketone,
targeted molecular weight, number of passes under the UV lamp, amount of PPT
as the crosslinking reagent, and the concentrations of the initial solutions were
the main variables utilized in the construction of our DOE (Table 1).

Temperature of the inert chamber containing the solutions increased as it
was passed under the UV lamp. To prohibit any possible interference of
increasing temperature in the polymerization process, the chamber was allowed
to cool down between the passes.

After extensive drying, the resulting films were analyzed using variable
techniques. First, to understand their thermal decomposition behaviors we performed thermo gravimetric analysis (TGA) on each film sample. According to
these studies, films were mostly dry. Also, we were able to obtain the onset
decomposition temperature, Td, for each film from the TGA analysis data (Figure
2).

Additionally, we used differential scanning calorimetry (DSC) to obtain
the glass transition temperatures, Tg, for our samples (Figure 2). Another
important data that we obtained from these experiments was the extent of the

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reacted monomers. We did not observe any sharp melting exotherms for the starting diketones suggesting the photopolymerization process was successful. In addition, we were able to obtain if any unreacted acrylate sites were left by checking the endotherms for thermal self-polymerization.

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<th>PPT (%)</th>
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Table 1. Tabular demonstration of the parameters varied in DOE and the $T_i$s and $T_g$s obtained for the resulting polymer films.

To better understand the film properties in terms of experimental conditions, statistical analysis was performed on the data presented in Table 1. For each diketone, strong correlations between $T_i$, reaction concentration, and amount of PPT crosslinking reagent were noted (Figure 2). Interestingly, the formulated molecular weight was not significant in the model. Ongoing statistical modeling is probing the value of this and other observations.

![Figure 2](image)

Figure 2. Statistical correlation between $T_i$, PPT (%) and conc. (%) obtained for the polymer films photocured by 35 passes.

Conclusions

Irradiation of o-methylphenyl functionalized ketones generates photocured that can be trapped by acrylic esters through Diels-Alder cycloadditions. This methodology can be extended to create thin polymer film as a novel approach for photocured film development.

Polymer properties can be tuned by varying the photoreactive diketones. A series of diketones were synthesized to obtain films with varying properties. Currently, we are in the process of studying the data related to the resulting films. Our progress in this field will be reported in due course.

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References