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

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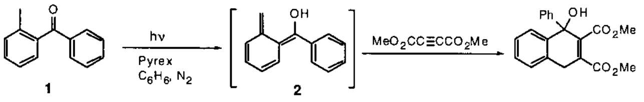
Introduction

Diels-Alder cycloadditions have often 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 polyimides, which employs o-quionodimethanes (o-QDMs), generated by a well-known photochemical reaction: the photoenolization of *o*-methylphenyl ketones.[2] Photolysis of *o*-methylbenzophenone **1** produces hydroxy-o-quino- dimethane **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 multi *o*-methylphenyl ketone functionalities. We further investigated these molecules as photoreactive monomers to obtain polyester films through Diels-Alder cycloadditions.[4]

Scheme 1



Experimental

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

Instrumentation ^{1}H and^{13}C NMR spectra of the ketones were obtained on a Bruker AC-200 spectrometer. $CDCl_3$ 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 NH_4Cl. The organic phase was collected and the aqueous phase extracted with THF. The organic extracts were combined and dried over Na_2SO_4. The solvent was dried in vacuo to yield the crude product. A (1:1) mixture of concentrated HCl and H_2O 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 CH_2Cl_2. 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 ^{1}H and ^{13}C NMR.

General Procedure for the Film Curing by Irradiation. A solution of the ketone, 1,6-hexanediol ethoxylate diacrylate (HED), pentaerythritol triacrylate (PPT) and methyl acrylate in cyclohexanone was prepared. This solution was transferred into a tin pan and placed in an inerting 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.

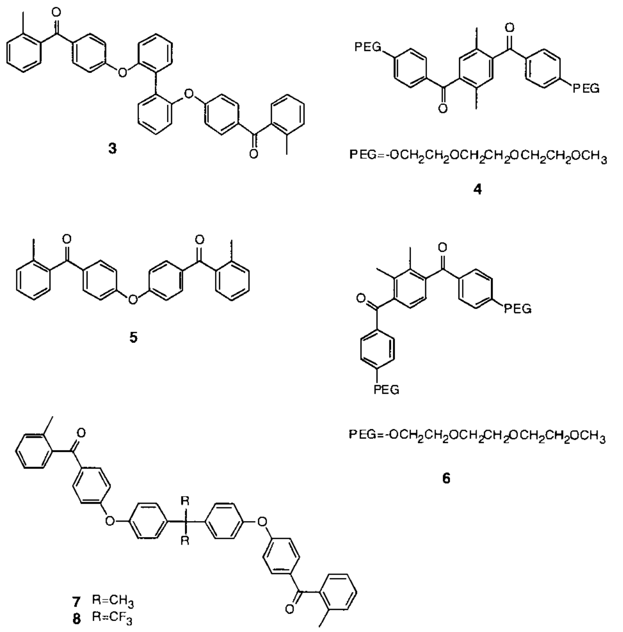


Figure 1. Structures of the diketone monomers (**3-8**).

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 dinitriles by Grignard synthesis with yields higher than 50%.

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

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 photoenol 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, T_d, for each film from the TGA analysis data (Figure 2).

Additionally, we used differential scanning calorimetry (DSC) to obtain the glass transition temperatures, T_g, for our samples (Figure 2). Another important data that we obtained from these experiments was the extent of the reacted monomers. We did not observe any sharp melting exotherms for the starting diketones suggesting the photoenolization 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.

Ketone	Conc. (%)	PPT (%)	# of passes	FMW ($x10^3$)	T_g (°C)	T_d (°C)
5	20	0	5	40	8.9	318
5	51	50	35	200	-0.7	382
6	20	50	35	200	-6.3	377
7	20	50	5	40	3.5	381
7	51	0	35	200	-11.2	416
3	20	0	5	200	4.8	357
4	51	50	5	200	-26.3	372
4	20	0	35	40	-12.9	390
8	20	0	5	200	7.9	365
8	51	50	35	40	-7.9	368
3	51	50	35	40	-7.8	370
6	51	0	35	200	-20.1	384
7	51	0	35	200	-3.3	398
7	20	50	5	40	4.7	379
6	51	0	5	40	-24.9	389
4	51	50	5	200	-27.7	379
3	51	0	5	40	2.98	360
4	20	0	35	40	-9.79	389

Table 1. Tabular demonstration of the parameters varied in DOE and the T_d'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_g, 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

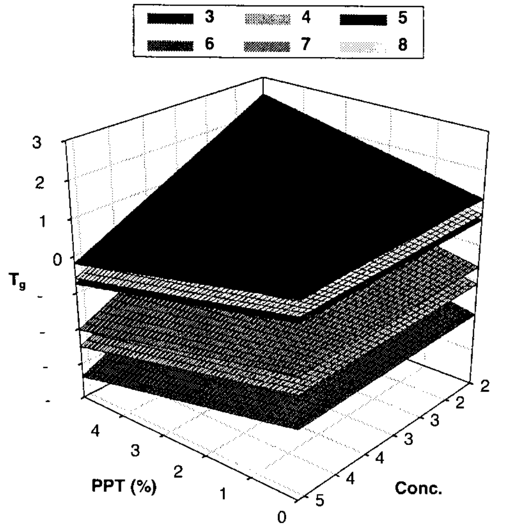


Figure 2. Statistical correlation between T_g, PPT (%) and conc. (%) obtained for the polymer films photocured by 35 passes.

Conclusions

Irradiation of o-methylphenyl functionalized ketones generates photoenols 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.

Acknowledgements. The authors of this paper would like to thank Daniel A. Scheiman for his help in analysis and characterization of the compounds.

References

(1) Stenzenberger, H.D.; In *Polyimides and Other High Temperature Polymers*; Abadie, M.J.; Sillion, B., Eds.; Elsevier: New York, **1991**, 215.

(2) Meador, M.A.B.; Williams, L.L.; Scheiman, D.A.; Meador, M.A., *Macromolecules,* **1996**, *29*, 8983.

(3) Yang, N.C.; Rivas, C.J, *J. Am. Chem. Soc.* **1961**, *83*, 2213.

(4) Meador, M.A. *NASA TM 89836*, **1987**.