Diels-Alder Trapping of Photochemically Generated *o*-Quinodimethane Intermediates: An Alternative Route to Photocured Polymer Film Development

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Abstract

Photolysis of *o*-methylphenyl ketones generates *bis*-*o*-quinodimethane intermediates that can be trapped *in situ* by dienophiles through Diels-Alder cycloadditions. This well-known photochemical process is applied to a series of six new photoreactive monomers containing *bis*-(*o*-methylphenyl ketone) functionalities combined with diacrylate and triacrylate ester monomers for the development of acrylic ester copolymer blends. Irradiation of cyclohexanone solutions of the *bis*-(*o*-methylphenyl ketone)s and acrylate esters produce thin polymer films. Solid state ^{13}C NMR data indicated 47-100% reaction of the *bis*-(*o*-methylphenyl ketone)s, depending on experimental conditions, to yield the desired products. DSC and TGA analyses were performed to determine the glass transition temperature, T_g, and onset of decomposition, T_d, of the resulting polymer films. A statistical Design of Experiments approach was used to obtain a systematic understanding of the effects of experimental variables on the extent of polymerization and the final polymer properties.

Keywords: *o*-Quinodimethane, Photoenol, Diels-Alder trapping, Photocured copolymers, Acrylic esters.

Introduction

Diels-Alder cycloadditions have often been utilized in polymer synthesis as an alternative to condensation reactions.[1] Previously,[2] our group developed a method for the preparation of linear aromatic polyimides by exploiting Diels-Alder cycloaddition reactions of *bis*-*o*-quinodimethanes, which are generated *in situ* by a well-known photochemical reaction: the photoenolization of *o*-methylphenyl ketones.[3] As depicted in Scheme 1, photolysis of *o*-methylbenzophenone **(1)** produces a pair of hydroxy-*o*-quinodimethane isomers **(3Z** and **3E)** via a 1,4-biradical intermediate **(2)**. The quinodimethane isomer, **3E,** is unstable and reverts to the starting material with high efficiency. **3Z** can be trapped with dienophiles, such as dimethyl acetylenedicarboxylate **(3d)**, to produce the corresponding cycloadduct.[4]

Herein, we report an extension of this approach toward development of photocured polymer films using acrylic ester diacrylates and triacrylates, and *bis*-(*o*-methylphenyl ketone)s as monomers. A series of molecules with bis-(*o*-methylphenyl ketone) functionalities was synthesized (Table 1, **5-10**) and characterized by standard analytical techniques (see Experimental Section). UV irradiation of these photoreactive monomers in the presence of diacrylates and triacrylates produced polymer blends via Diels-Alder cycloadditions of the photoenols. Physical properties (T_g and T_d) of the resulting polymer films, as well as the extent of reaction of the *bis*-(*o*-methylphenyl ketone)s, were shown to be systematically dependent on the reaction conditions.

Experimental Section

Materials. 1,6-Hexanediol ethoxylate diacrylate **(11)**, pentaerythritol triacrylate **(12)** and methyl acrylate **(13)** were purchased from the Aldrich Chemical Company and stored in the dark at less than 10 °C. Tetrahydrofuran (THF) was obtained from Aldrich and purified by distillation using potassium/benzophenone as drying agents. Triethylene glycol monomethyl ether tosylate (PEG-TOS) was prepared according to a literature procedure.[5] All other reagents were purchased from commercial sources and used without further purification.

General Synthesis of Dinitriles (*A*). Phenol or bisphenol (1 eq., ca. 1 mol) was dissolved in dimethylsulfoxide (DMSO) (100 mL) in a 500 mL, 3 neck round bottom flask equipped with a Dean-Stark trap, a condenser, and nitrogen inlet. Anhydrous K_2CO_3 (1 eq., ca. 1 mol) and 100 mL of benzene were added. The mixture was heated (90 °C) with stirring for 18 h or until the level of collected water became constant. The remaining benzene was removed by distillation and the reaction mixture was allowed to cool to room temperature. 4-Nitrobenzonitrile (1 or 2 eq., ca. 1 or 2 mol) was added directly to the reaction flask. The reaction was stirred at 100 °C for 72 h, and then allowed to cool to room temperature. The resulting mixture was poured into a flask containing 1L of distilled water. The flask was cooled in an ice bath and the product was allowed to precipitate overnight. The crude product was then filtered and dried under vacuum. The resulting solid was recrystallized from hot ethanol and dried under vacuum.

4,4'-dicyanodipheny ether (7a). 50% yield (m.p. 179-181 °C). ^1H (200 MHz, $CDCl_3$): δ 6.94 (d, J = 8 Hz, 2H), 7.50 (d, J = 8 Hz, 2H).

2,2'-*bis* (4-cyanophenoxy)biphenyl (8a). 33% yield (m.p. 145-147 °C). ^1H (200 MHz, $CDCl_3$): δ 6.62 (d, J = 8 Hz, 4H), 6.81 (d, J = 8 Hz, 2H), 702-7.19 (m, 6H), 7.28 (d, J = 8 Hz, 4H).

2,2-bis(2-(4-cyanophenoxy)phenyl) propane (9a). 79% yield (m.p. 122-124 °C). ^1H (200 MHz, $CDCl_3$): δ 1.68 (s, 6H), 6.85 (m, 8H), 7.09 (d, J = 8 Hz, 4H), 7.40 (d, J = 8 Hz, 4H).

2,2-bis(2(4-cyanophenoxy)phenyl)-1,1,1,3,3,3-hexafluoropropane (10a). 90% yield (m.p. 161-163 °C). ^1H (200 MHz, $CDCl_3$): δ 7.04 (m, 8H), 7.38 (d, J = 8 Hz, 4H), 7.59 (d, J = 8 Hz, 4H).

General Synthesis of Diketones (*B*). To a stirred solution of the corresponding dinitrile in dry THF under nitrogen was added dropwise a THF solution of either 4-methoxy phenylmagnesium bromide (reaction B_1) or 2-methyl phenylmagnesium bromide (reaction B_2). The resulting mixture was refluxed under nitrogen for 18 h. The reaction mixture was then allowed to cool to room temperature and poured into a saturated aqueous NH_4Cl solution. 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 water was added to that product and the resulting mixture was refluxed for 18 h. The mixture was then cooled to room temperature and extracted with CH_2Cl_2. The combined organic extracts were washed with a 5% aqueous NaOH solution. The solvent was dried to yield the crude product. Products were further purified either by recrystallization or column chromatography.

2,5-*bis*(4-methoxybenzoyl)-*p*-xylene (5a).[5] Washing with methanol, followed by recrystallization from ethanol afforded the cream colored product in 63% yield (m.p. 181-182 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.24 (s, 6H), 3.88 (s, 6H), 6.92 (d, J = 8 Hz, 4H), 7.16 (s, 2H), 7.79 (d, J = 8 Hz, 2H).

2,5-*bis*(4-methoxybenzoyl)-*o*-xylene (6a). Washing with methanol, followed by recrystallization from ethanol afforded cream colored product in 70% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.18 (s, 6H), 3.86 (s, 6H), 6.90 (d, J = 8 Hz, 4H), 7.14 (s, 2H), 7.78 (d, J = 8 Hz, 4H).

4,4'-bis(2-methylbenzoyl) diphenyl ether (7). Column chromatography (12:1 gradient to 5:1 hexane:ethyl acetate) gave the product in 40% yield as a white solid (m.p. 80-81 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.32 (s, 6H), 7.05 (d, J = 8 Hz, 4H), 7.23-7.38 (m, 8H), 7.81 (d, J = 8 Hz, 4H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 197.43, 160.51, 138.78, 136.84, 133.78, 132.86, 131.31, 130.51, 128.51, 125.51, 119.00, 20.20. Mass (m/z): 406.5 calcd., 407.2 found. IR (KBr, cm^{-1}): 3094.0, 3064.4, 3010.0, 2954.0, 2922.5, 2860.0, 1655.2, 1584.2, 1499.7, 1485.6, 1452.8, 1421.0, 1310.6, 1293.8, 1251.0, 1171.3, 1149.5, 1109.4. Calculated for $C_{28}H_{22}O_3$: C 82.64, H 5.46. Found: C 82.50, H 5.45.

2,2'-*bis*(4-(2-methylbenzoyl)phenoxy)biphenyl (8). Column chromatography (6:1 hexane:ethyl acetate) gave a white solid in 81% yield (m.p. 58-60 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 6H), 6.82 (d, $J = 10$ Hz, 4H), 7.01 (d, $J = 10$ Hz, 2H), 7.20-7.42 (m, 14H), 7.66 (d, $J = 10$ Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 197.17, 161.91, 152.99, 138.91, 136.34, 132.19, 132.07, 130.92, 130.05, 129.99, 129.34, 128.07, 125.22, 124.56, 120.12, 117.28, 19.84. Mass (m/z): 574.7 calcd., 575.4 found. IR (KBr, cm^{-1}): 3060.7, 3021.2, 2925.2, 1659.6, 1599.0, 1577.9, 1499.3, 1473.7, 1427.2, 1306.4, 1292.1, 1254.3, 1240.0, 1198.0, 1169.0, 1149.1, 1110.8. Calculated for $C_{40}H_{30}O_4$: C 83.60, H 5.26. Found: C 83.37, H 5.28.

2,2-bis(2-(4-(2-methylbenzoyl)phenoxy)phenyl)propane (9). Column chromatography (6:1 to 4.5:1 hexane:ethyl acetate) gave a white solid in 44% yield (m.p. 56-59 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74 (s, 6H), 2.34 (s, 6H), 7.02 (d, $J = 10$ Hz, 8H), 7.26-7.42 (m, 12H), 7.95 (d, $J = 10$ Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 197.19, 162.25, 153.63, 146.89, 138.95, 136.31, 132.43, 132.51, 130.89, 129.95, 128.34, 128.03, 125.17, 119.72, 117.11, 42.39, 30.99, 19.80. Mass (m/z): 616.7 calcd., 617.3 found. IR (KBr, cm^{-1}): 3059.0, 3037.6, 2966.5, 2927.3, 2871.4, 1659.8, 1591.2, 1597.7, 1451.5, 1405.6, 1383.6, 1363.6, 1307.1, 1291.5, 1269.4, 1240.0, 1206.1, 1170.2, 1148.3, 1108.8, 1080.5, 1013.6. Calculated for $C_{44}H_{36}O_4$: C 83.74, H 5.88. Found: C 83.44, H 5.87.

2,2-bis(2-(4-(2-methylbenzoyl)phenoxy)phenyl-1,1,1,3,3,3-hexafluoropropane (10). Column chromatography (6:1 hexane:ethyl acetate) followed by ethanol digestion produced the target product as a white solid in 24% yield (m.p. 148 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.31 (s, 6H), 7.03 (d, $J = 8$ Hz, 8H), 7.22-7.42 (m, 12H), 7.79 (d, $J = 8$ Hz, 4H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 197.43, 161.01, 156.66, 138.88, 138.81, 136.72, 133.35, 133.29, 132.88, 132.21, 131.22, 130.39, 129.15, 128.38, 125.48, 119.28, 118.44, 20.16. Mass (m/z): 724.7 calcd., 725.3 found. IR (KBr, cm^{-1}): 3070.3, 3019.3, 2970.8, 2927.6, 1656.5, 1594.4, 1510.1, 1500.0, 1455.5, 1418.1, 1380.6, 1294.6, 1245.0, 1206.1, 1173.8, 1149.6, 1135.6, 1112.8, 1018.0. Calculated for $C_{44}H_{30}O_4F_6$: C 71.27, H 4.13. Found: C 70.25, H 4.16.

General Deprotection (*C*). To a 250 mL round bottom flask, the methoxy protected diketone (10-20 mmol), 48% HBr in H_2O (100 mL), and 50 mL acetic acid were added. The mixture was refluxed for 18 h then allowed to cool to room temperature. The reaction mixture was then added to 200 mL of cold water and filtered to collect the cream colored solid product.

2,5-*bis*(*p*-hydroxybenzoyl)-*p*-xylene (5b).[5] Recrystallization from methanol gave the title compound as a white solid in a yield of 77% (m.p. 296-299 °C). ^{1}H NMR (200 MHz, d_6-DMSO): δ 2.16 (s, 6H), 6.89 (d, *J* = 8 Hz, 4H), 7.21 (s, 2H), 7.65 (d, *J* = 8 Hz, 2H), 10.59 (broad s, 2H).

2,5-*bis*(*p*-hydroxbenzoyl)-*o*-xylene (6b). The crude product was dissolved in hot methanol, filtered to remove insoluble impurities, and evaporated to dryness. The white compound was recovered in 91% yield (m.p. 258-262 °C). ^{1}H NMR (200 MHz, d_6-DMSO): δ 2.10 (s, 6H), 6.88 (d, *J* = 8 Hz, 4H), 7.15 (s, 2H), 7.63 (d, *J* = 8 Hz, 4H), 10.58 (s, 2H).

General Addition of PEG (*D*). To a 200 mL round bottom flask, the deprotected diketone (1 eq., ca. 9 mmol), K_2CO_3 (3 eq., ca. 27 mmol) and dimethylformamide (DMF) (30 mL) were added. The mixture was stirred at 55 °C for 0.5 h under N_2 and a solution PEG-TOS (2 eq., ca. 18 mmol) in 10 mL of DMF was added dropwise. The resulting mixture was stirred at 75 °C for 18 h and then cooled to room temperature. The solvent was evaporated *in vacuo* and 150 mL of diethyl ether was added to the resulting crude product. The organic extract was then washed with H_2O (2x30 mL), 5% solution of aqueous NaOH (2x30 mL), and brine (2x30 mL) and finally dried over Na_2SO_4. Concentration *in vacuo* yielded yellow oil that solidified gradually to form the cream colored solid product.

2,5-*bis*(*p*-(tetra(ethyleneglycol)oxy)benzoyl)-*p*-xylene (5).[5] 86% yield (m.p. 54-55 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.24 (s, 6H), 3.38 (s, 6H), 3.50-3.73 (m, 16H), 3.89 (t, *J* = 2 Hz, 4H), 4.21 (t, *J* = 2

Hz, 4H), 6.94 (d, $J = 10$ Hz, 4H), 7.17 (s, 2H), 7.78 (d, $J = 10$ Hz, 4H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 196.83, 163.18, 140.61, 132.88, 132.41, 130.23, 129.80, 114.40, 71.45, 70.86, 70.62, 70.53, 69.45, 67.71, 58.94, 19.09. Mass (m/z): 638.7 calcd., 639.4 found. IR (KBr, cm^{-1}): 2926.2, 2870.7, 2816.7, 1652.3, 1600.5, 1573.9, 1509.1, 1467.3, 1455.6, 1423.3, 1387.5, 1351.3, 1312.2, 1298.5, 1283.9, 1252.0, 1217.0, 1197.1, 1174.5, 1146.0, 1133.4, 1100.9, 1073.2, 1054.3, 1029.5. Calculated for $C_{36}H_{46}O_{10}$: C 67.92, H 7.26. Found: C 67.87, H 7.24.

2,5-*bis*(*p*-(tetra(ethyleneglycol)oxy)benzoyl)-*o*-xylene (6). 86% yield (m.p. 49-50 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.20 (s, 6H), 3.38 (s, 6H), 3.50-3.70 (m, 16H), 3.89 (t, $J = 2$ Hz, 4H), 4.21 (t, $J = 2$ Hz, 4H), 6.96 (d, $J = 10$ Hz, 4H), 7.16 (s, 2H), 7.82 (d, $J = 10$ Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 197.51, 163.19, 141.06, 135.07, 132.60, 130.16, 124.21, 114.27, 71.86, 70.84, 70.56, 69.42, 67.66, 59.02, 16.91. Mass (m/z): 638.7 calcd., 639.4 found. IR (KBr, cm^{-1}): 2873.7, 2822.1, 1648.4, 1599.7, 1573.6, 1508.5, 1459.3, 1421.6, 1402.8, 1399.0, 1351.4, 1311.5, 1298.9, 1252.0, 1202.3, 1166.2, 1132.3, 1102.0, 1057.0, 1031.6. Calculated for $C_{36}H_{46}O_{10}$: C 67.92, H 7.26. Found: C 67.72, H 7.26.

Characterization. ^{1}H and ^{13}C NMR spectra of the ketones were obtained on a Bruker AC 200 or Avance 300 MHz spectrometer. $CDCl_3$ or d_6-DMSO containing TMS as an internal reference was used as the solvent for solution spectra as indicated. Solid ^{13}C NMR data was acquired on a Bruker Avance 300 spectrometer using cross-polarization and magic angle spinning at a rate of 7 kHz. A TOSS routine was employed to suppress spinning side bands. Solid spectra were externally referenced to the carbonyl of glycine which appears at 176.1 relative to TMS. 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. IR spectra of monomers were recorded in KBr pellets using a Nicolet 510P FTIR spectrophotometer. Mass spectral data were measured on a Finnegan LCQ (atmospheric pressure ionization) in positive ion mode with an inlet temperature of 180-220 °C. DSC experiments were run on a modulated

(± 0.5 °C/40 s) TA Instruments Q1000. The heating profile was set to 5 °C/min and run from -90 to 300 °C under nitrogen atmosphere. TGA data was collected on a TA Instruments model 1000, under nitrogen atmosphere, and with a ramp rate of 5 °C/min from room temperature to 750 °C.

Film Preparation. A solution of the appropriate *bis*-(*o*-methylphenyl ketone) (**5-10**), 1,6-hexanediol ethoxylate diacrylate (HED, **11**), pentaerythritol triacrylate (PPT, **12**) and methyl acrylate (**13**) in cyclohexanone was transferred into a standard aluminum weighing 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, a Fusion UV Systems HP-6. The UV lamp intensity was set at 65% and the belt speed at 2 (approx. 2 min per pass). After each pass the chamber was allowed to cool for 2 minutes. Resulting materials were further dried in a vacuum oven at 55 °C for 96 h then 90 °C for 24 h.

Results and Discussion

A series of diketones (**5-10**) was used in this study in which two *o*-methylbenzoyl moieties were connected by linking groups of various lengths, flexibility and geometry (linear, kinked and twisted) as shown in Table 1. All diketones were synthesized from the precursor dinitriles by standard Grignard reactions in moderate to high yield. Diketones **5** and **6** were further functionalized with triethylene glycol monomethyl ether units for the purpose of improved solubility in cyclohexanone. All diketones were characterized by standard techniques, including ^{1}H and ^{13}C NMR, mass spectroscopy, and elemental analysis. 1,6-Hexanediol ethoxylate diacrylate (HED, **11**) was used as a bis-dienophile in these studies (Scheme 2). The long alkyl chain associated with this monomer contributes to the molecular mobility in the system, compensating for the loss of entropy due to chain extension. Pentaerythritol triacrylate (PPT, **12**) was used as a tris-dienophile to obtain higher glass transition temperatures by the introduction of crosslinking or branching. Methyl acrylate (**13**) was used in all cases as an end-cap to control polymer molecular weight.

All polymer films prepared in this study were from monomer solutions in cyclohexanone. Cyclohexanone, a solvent with a high boiling point, minimizes the possibility of evaporation that can affect the degree of polymerization by uncontrollably varying the concentrations of the solutions. In addition, earlier studies demonstrated that cyclohexanone does not interfere with the desired photoenol formation step.

The temperature of the inerting chamber containing the solutions increased as it was passed under the UV lamp. To minimize this temperature increase during polymerization, the chamber was allowed to cool under ambient conditions for 2 minutes between passes. It is important to note, however, that the cooling process was not suitably efficient and the temperature increased somewhat after each pass. Therefore, under our experimental conditions, thermal acrylate polymerization was a competing reaction.[7] This was confirmed by a control experiment in which the acrylate monomer by itself was irradiated in cyclohexanone solution under the same experimental conditions and was indeed observed to polymerize. Nevertheless, quantitative NMR experiments (*vide infra*) reveal 47-100% reaction of the *bis*-(*o*-methylphenyl ketone)s, depending on experimental conditions and specific diketone. These data suggest the formation of copolymers with varying degrees of *bis*-(*o*-methylphenyl ketone) incorporation.

After extensive drying, the resulting films were analyzed using various techniques. The onset of decomposition, T_d, for each film was measured in N_2 by TGA analysis. Differential scanning calorimetry (DSC) was used to obtain the glass transition temperatures, T_g, for all films.

Solid ^{13}C NMR spectroscopy was performed to probe the extent of reaction of the *bis*-(*o*-methylphenyl ketone)s. Typical solid ^{13}C NMR spectra of the resulting films, as shown in Figure 1, contained aliphatic peaks (a: 20-50 ppm), ethylene glycol peaks (b: 60-80 ppm), aromatic peaks (c: 110-165 ppm), and two carbonyl peaks (d: 170-180 and e: 195-200 ppm). The latter is of particular interest due to the presence of two distinct carbonyl resonances. The signal at 195 ppm can be assigned to unreacted diketone while the other, a broad band at 175 ppm, represents both unreacted and reacted acrylate.

Multiple contact time experiments demonstrated that these two carbonyl peaks maintained the same ratio of peak size regardless of condition, thus allowing them to be integrated together. Initial experimental conditions were designed to include an equimolar ratio of reactive sites (i.e. one *o*-methylphenyl ketone moiety for every one acrylic ester). This design feature allowed integration of carbonyl signal intensities and direct calculation of the percent reaction of the *bis*-(*o*-methylphenyl ketone)s. For example, the polymer film from run 4, diketone **9**, displayed a carbonyl signal for unreacted *bis*-(*o*-methylphenyl ketone) near 195 ppm that integrated to 0.22. A second signal near 175 ppm corresponding to the acrylate (reacted and unreacted) carbonyls was integrated to 1.00. This data may be interpreted as 22% unreacted *bis*-(*o*-methylphenyl ketone), or a reaction extent of 78%.

A statistical Design of Experiments approach was used to assess the effects of photopolymerization conditions on the degree of polymerization and selected properties of the polymer films produced from each of the *bis*-(*o*-methylphenyl ketone)s (*k*) studied. Four additional variables were chosen, including number of passes (*p*) under the UV lamp, concentration of the initial solution (*s*) in weight percent of monomers in cyclohexanone, formulated molecular weight (*f*), and percent of triacrylate (*t*) as a fraction of the total acrylates. A linear model of the following form was entertained:

$$Response = \mathrm{A} + \mathrm{B}p + \mathrm{C}s + \mathrm{D}t + \mathrm{E}k + \mathrm{F}f + \mathrm{G}ps + \mathrm{H}pt + \mathrm{I}pk + \mathrm{K}pf + \mathrm{L}st + \mathrm{M}sk + \mathrm{N}sf + \mathrm{O}tk + \mathrm{P}tf + \mathrm{Q}kf$$

where A through Q are coefficients empirically derived from experimental data and *Response* is either T_d, T_g, or extent of reaction. The model contains terms for first order effects of all five variables as well as all two way interaction terms for *p*, *s*, *t*, *k* and *f*. To evaluate linear effects of *p*, *s*, *t*, and *f*, a minimum of two levels of each variable must be considered. The two levels of *p* used were 5 and 35 passes. Solution concentration (*s*) was evaluated at 20 to 51% monomer content by weight. The amount of PPT (*t*) as a cross link was evaluated at 0 and 50% of the diacrylate concentration (and concomitantly diacrylate was varied from 100 to 50%). Formulated molecular weight (*f*) was evaluated at 40,000 or 200,000 g/mol. Additionally, there are six levels of the discrete variable diketone, or *k*, namely all of the *bis*-(*o*-methylphenyl ketone)s **(5-10)**.

Evaluation of the model using a full-factorial design would require 96 experiments, plus several repeats to assess model accuracy and reproducibility. To minimize the number of experiments in the screening study,[8] a *d*-optimal experimental design strategy was chosen. In this type of non-classical design, a set of runs is computer-generated from the 96 candidate runs to evaluate the desired model most efficiently.[9] The scope of the design can be described using a three-dimensional box (Figure 2). The three axes of the box represent three continuous variables (*s*, *t* and *f*). The numbers in the box represent each of the six diketones and are positioned according to the conditions of the experimental run. The remaining continuous variable (*p*) is represented by the color scheme. The total number of unique experiments shown in the *d*-optimal design is 18. In addition, 4 runs from across the design were repeated to assess model reliability and accuracy, assuming error is consistent across the whole design. Table 2 shows the random order of the 22 total film-curing experiments along with the corresponding experimental data.

A mathematical model for each of the three experimental results (T_d, T_g, and extent of reaction) was derived using multiple linear least-squares regression.[9] All independent variables were transformed to the -1 to 1 range prior to modeling to minimize correlation among terms. Terms deemed not to be statistically significant (<90% confidence) were dropped from the model one at a time by the stepwise modeling technique. Each model included all variables as independent terms and/or interactive terms. Linear response surfaces for each of the diketones were generated and stacked in three dimensions (response vs. variable 1 vs. variable 2, while holding the other three variables constant). Below are selected examples of response surface models for T_d, T_g, and extent of reaction with related discussion.

Extent of reaction is reported as the percent diketone consumed. Significant terms in the model included first-order effects of formulated molecular weight (*f*) and number of passes (*p*) under the UV lamp. Two interactive/synergistic effects of type of diketone with number of passes (*k*p*), percent triacrylate with initial solution concentration (*t*s*), and formulated molecular weight with total monomer weight percent (*f*s*) were also significant. Standard error of regression for the model was 3.62% with an $r^2 = 0.974$.

Figure 3 shows a response surface model of the extent of reaction graphed vs. initial concentration (*s*) and percent triacrylate (*t*). Diketones **6** and **5** had the greatest extent of reaction over all the diketones studied, followed by **8** then **10**. Diketones **9** and **7** at best showed only 80% conversion of diketone. For any diketone studied and at either level of *t*, increasing *s* leads to greater diketone incorporation. Diels-Alder trapping of photoenols by acrylate, (*vide supra*) is in competition with self-polymerization of the acrylates. Since the Diels-Alder cyclopolymerization process is a bimolecular reaction, increasing the concentration of both monomers will increase the effective rate constant for Diels-Alder cyclopolymerization leading to a higher extent of reaction and incorporation of the short lived photoenols.[4] The rate constant for Diels-Alder trapping of *o*-methylbenzophenone derived photoenol with maleic anhydride in acetonitrile is reported to be 2.2×10^6 M/s.[5]

Also evident in Figure 3 is the interactive effect between initial monomer concentration and percent of triacrylate (s**t*). At 0% *t*, increasing *s* has a large effect on increasing extent of reaction. However, at 50% *t*, the effect is much less pronounced. This trend is likely due to inhibited intermolecular interactions caused by greater extent of crosslinking.

Selected response surfaces of extent of reaction graphed vs. total monomer weight percent (*s*) and number of passes (*p*) are presented in Figure 4 with *t* held constant at 50% for both graphs, and formulated molecular weight (*f*) at 40,000 g/mol (bottom) and 200,000 g/mol (top). Most noticeable is the interaction between diketone type and number of passes (*k*p*). Increasing the number of passes dramatically increases the incorporation of diketone into the polymer films for **5**, **6**, **8**, and **10** while there is very little enhancement for **7** or **9**. It should be noted that number of passes directly corresponds to reaction time (i.e. amount of irradiation). During photoenol trapping, the reactive intermediate has a finite existence that requires interaction with the dieneophile before it is consumed by other reactive pathways.[4] Consequently, increased irradiation time enhances reaction efficiency as long as the *bis*-(*o*-methylphenyl ketone)s maintain their mobility. Thus, the major effect of **5** and **6** on the extent of reaction may be rationalized by increased solubility (and likely mobility) imparted by the PEG units. The major effect of **8** and **10** on extent of reaction may also be due to increased mobility. Insertion of a nonlinear biphenyl (**8**) into otherwise linear structures is known to impart mobility in related polymers.[10] Also, the use of hexafluoroisopropylidene (**10**) has been documented to increase solubility in polymeric materials.[10]

A comparison of the top and bottom graphs in Figure 4 clearly demonstrates the interactive effect between solids concentration and formulated molecular weight (f*s) on extent of reaction. Low formulated molecular weight runs (bottom) show an increase in extent of reaction as initial solids concentration decreases while high formulated molecular weight runs are relatively insensitive to concentration effects.

Significant terms in the model for the onset of decomposition, T_d, include first-order effects of formulated molecular weight (f), number of passes (p) under the UV lamp, amount of PPT (t) as the crosslinking reagent, and the initial concentration (s). Synergistic/interactive effects including formulated molecular weight with triacrylate concentration ($f*t$) and initial concentration with number of passes ($s*p$) were also significant. Standard error of regression for the model was 5.47 °C with an $r^2 = 0.961$.

A graph of the response surface for T_d vs. number of passes (p) and initial concentration (s) is presented in Figure 5 (top). For all diketones, the combination of 5 passes and low initial concentration gives films with the lower onsets of decomposition. As the number of passes *or* the initial concentration content is increased, the T_d of the resulting films is increased. But with the largest number of passes and the highest initial concentration, the T_d is again decreased.

Inspection of the corresponding extent of reaction surface (Figure 5, bottom), provides insight into the reaction of the *bis*-(*o*-methylphenyl ketone)s under the identical experimental parameters discussed above. This graph shows a maximum extent of reaction of the *bis*-(*o*-methylphenyl ketone) for films produced with the highest initial solids concentration and 35 passes. However, short-term thermal stability (or T_d) of these films is lower than for samples produced with either low initial concentration *or* low number of passes. Under this extreme condition (high initial concentration and prolonged irradiation), it is reasonable to suggest an increase of thermal acrylate polymerization, not detectable by NMR, is the reason for the shift in T_d data.

Short term stability of polymer films made from the various diketones follows the order **9** > **6** ≈ **5** ≈ **10** > **8** >> **7** based on highest to lowest onset of decomposition. With the exception of diketone **9**, this roughly follows the observation that the higher the extent of reaction of the diketone the more stable the films. Curiously, diketone **9** has the highest T_d even though it is similar to diketone **7** in extent of reaction. Inspection of the *bis*-(*o*-methylphenyl ketone)s in Table 1 reveals **9** as a larger molecule with more aromatic content as compared to **7**. This structural difference likely enhances the higher short term thermal stability of polymers prepared from **9**.

Significant terms in the model for T_g data included first-order effects of formulated molecular weight (f), number of passes (p), percent triacrylate (t), and initial concentration (s). Interactive/synergistic effects of type of *bis*-(*o*-methylphenyl ketone) and number of passes ($k*p$) as well as amount of triacrylate and monomer solids content ($t*s$) and triacrylate and formulated molecular weight ($t*f$) were also significant. Standard error of regression for the model was 2.96 °C with an $r^2 = 0.997$.

A response surface model for T_g is presented in Figure 6. The PEG-functionalized *bis*-(*o*-methylphenyl ketone)s, **5** and **6**, as expected, possess low glass transition temperatures ranging from -20 to 0 °C, while the more aromatic diketones 7-10 have T_g all in excess of 20 °C. Most evident on the graph in Figure 6 is the effect of percent triacrylate on the T_g. As t increases and s decreases, the temperature of the glass transition increases, typically imparting as much as a 20 °C increase in T_g.

Conclusions

Irradiation of *bis*-(*o*-methylphenyl ketone)s generate photoenols that can be trapped by acrylic esters through Diels-Alder cycloadditions. By utilizing diacrylate and triacrylate dieneophiles to promote photoenol trapping, copolymer blends may be produced. This approach represents a novel process for photocured film development. A series of six new *bis*-(*o*-methylphenyl ketone)s, **5-10**, were synthesized and evaluated for copolymer film production. Physical properties of the resulting materials were altered by varying the photoreactive diketones and photocuring conditions. A statistically derived screening study was carried out to examine the effects of photocuring conditions for all six diketones on glass transition temperature, decomposition temperature, and extent of reaction. The resulting empirical models provided significant insight into the relationship between the reaction variables. In general, films derived from diketones with either attached PEG groups (**5** and **6**) or linking groups which impart extra molecular mobility (**8** and **10**), had a higher extent of reaction with increased time, presumably because of better solubility. Further studies will concentrate on refining the conditions for trapping the photoenols for these diketones. In addition, continuing efforts are underway to eliminate the competing acrylate polymerization which contributes to a drop in decomposition temperature and T_g.

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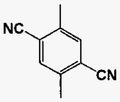
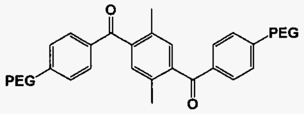
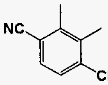
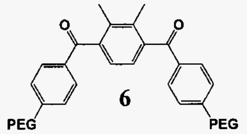
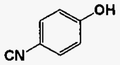
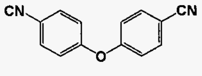
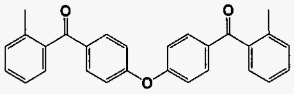
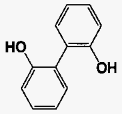
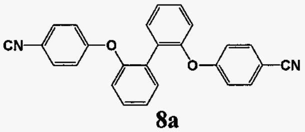
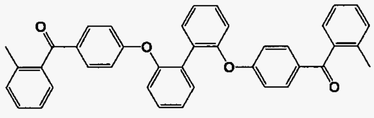
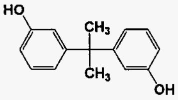
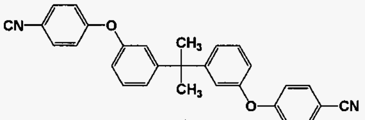
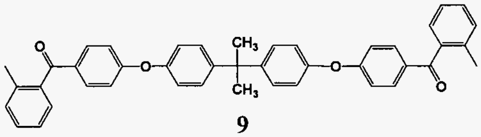
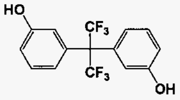
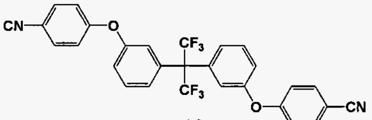
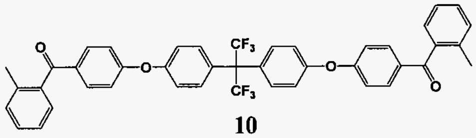
Table 1. Tabulated synthetic methodology.

Starting Material	Rx	Dinitrile	Rx[a]	*bis*-(*o*-Methylphenyl Ketone)[b]
---	---		***B₁*** **(5a)** ***C*** **(5b)** ***D***	 **5**
---	---		***B₁*** **(6a)** ***C*** **(6b)** ***D***	 **6**
	***A***	 **7a**	***B₂***	 **7**
	***A***	 **8a**	***B₂***	 **8**
	***A***	 **9a**	***B₂***	 **9**
	***A***	 **10a**	***B₂***	 **10**

[a] Reaction description of **5** and **6** are shown in sequence. For example, **5** was synthesized from the appropriate dinitrile using a three step procedure; ***B₁*** produces **5a**, ***C*** gives **5b**, and ***D*** affords the final product **5**.

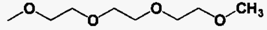
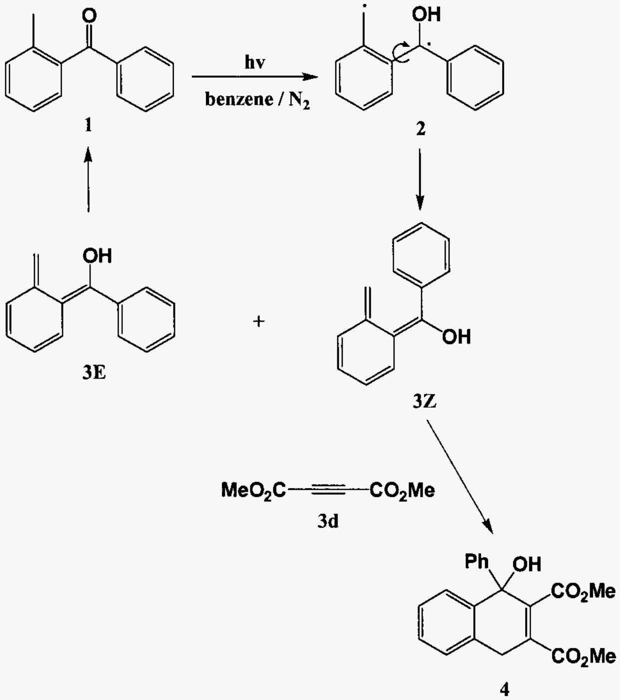
[b] PEG = 

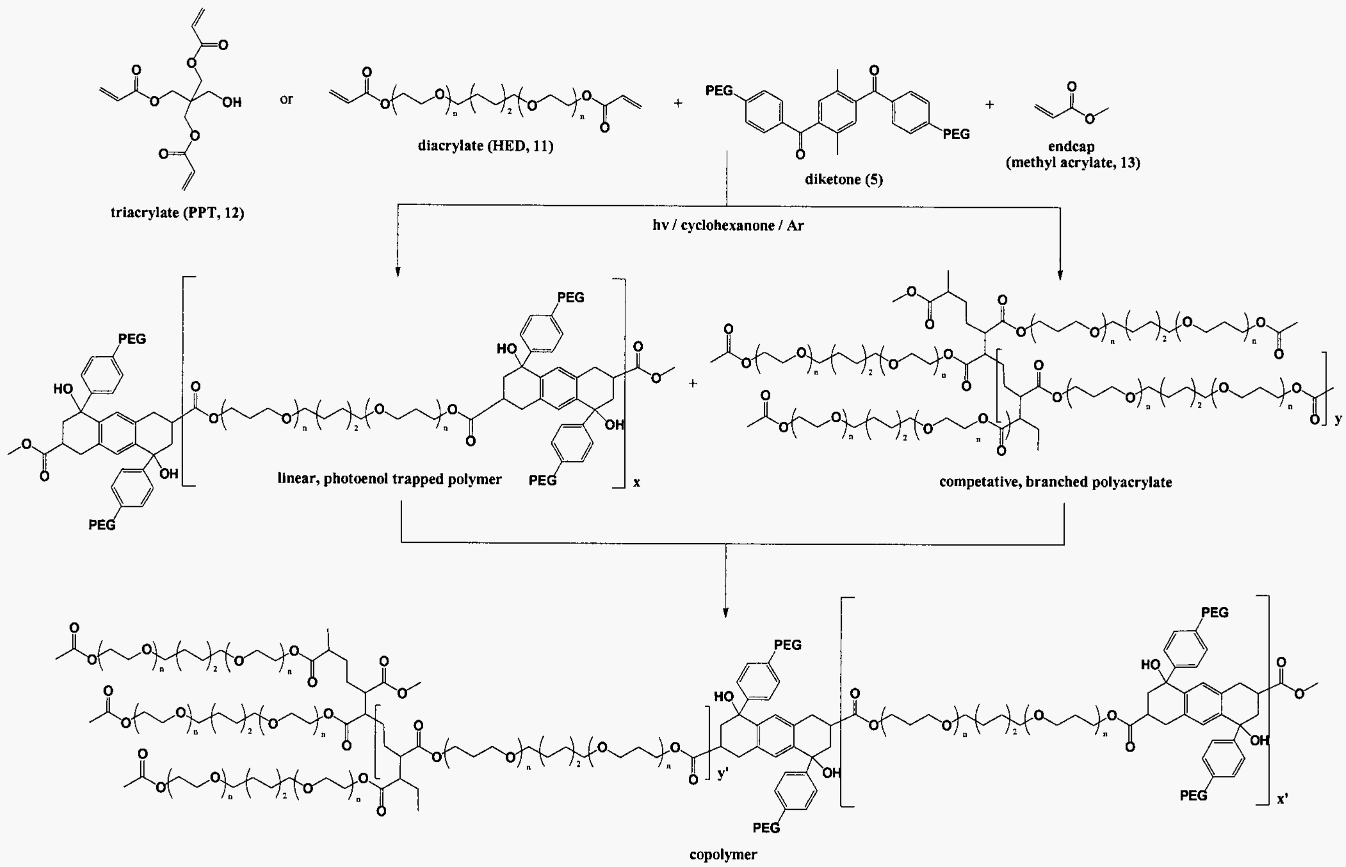
Table 2. Experimental design and corresponding data for copolymer films containing **5-10**.

Run	Diketone (*k*)	Conc. % (*s*)[a]	PPT % (*t*)[b]	# of Passes (*p*)[c]	FMW (x10^3,*f*)	T_g (°C)	T_d (°C)	Extent of Rx (%)[d]
1	**7**	20	0	5	40	13.9	294	74
2	**7**	51	50	35	200	22.8	293	75
3	**5**	20	50	35	200	2.6	338	92
4	**9**	20	50	5	40	39.5	343	78
5	**9**	51	0	35	200	33.4	352	83
6	**8**	20	0	5	200	32.9	336	49
7	**6**	51	50	5	200	-23.3	331	47
8	**6**	20	0	35	40	-4.6	351	96
9	**10**	20	0	5	200	35.2	344	56
10	**10**	51	50	35	40	22.4	335	78
11	**8**	51	50	35	40	29.8	336	80
12	**5**	51	0	35	200	-19.7	341	100
13	**9**	51	0	35	200	32.2	353	85
14	**9**	20	50	5	40	36.2	340	69
15	**5**	51	0	5	40	-23.6	348	47
16	**6**	51	50	5	200	-27.3	340	53
17	**8**	51	0	5	40	30.2	327	46
18	**6**	20	0	35	40	1.2	337	88
19	7	20	0	35	200	35.6	323	71
20	7	20	50	5	200	16.2	287	78
21	7	20	50	35	40	33.6	314	71
22	**5**	20	0	35	40	-4.0	346	92

[a] Mass percent of reagents in the total mixture
[b] Percent of triacrylate with respect to reactive sites (i.e. two triacrylates equal three diacrylates)
[c] Belt setting of 2 (approx. 2 min per pass) with 2 min cool down between passes
[d] From NMR integration, see text for details



Scheme 1. Photoenolization of *o*-methylbenzophenone (**1**) and subsequent Diels-Alder trapping with dimethyl acetylenedicarboxylate (**3d**).



Scheme 2. A schematic representation of the photo-induced polymerization of a *bis-o*-methylphenyl ketone (**5** shown here) with 1,6-hexanediol ethoxylate diacrylate (HED, **11**) dieneophile and methyl acrylate (**13**) end-cap.

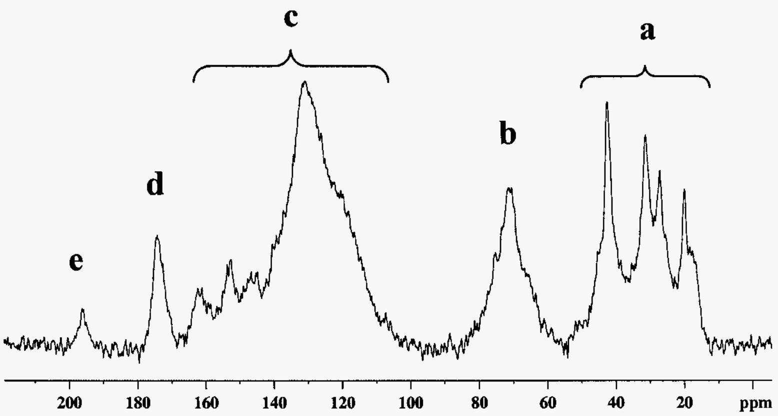


Figure 1. Representative ^{13}C NMR spectrum for a copolymer film. The figures corresponds to the *bis*-(*o*-methylphenyl ketone) **9** from experimental run 4.

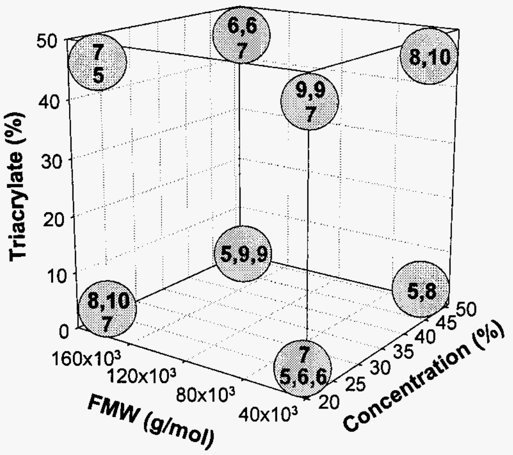


Figure 2. Plot of *bis*-(*o*-methylphenyl ketone)s run in the *d*-optimal experimental design. Black displays runs at $p = 5$ and red displays runs at $p = 35$.

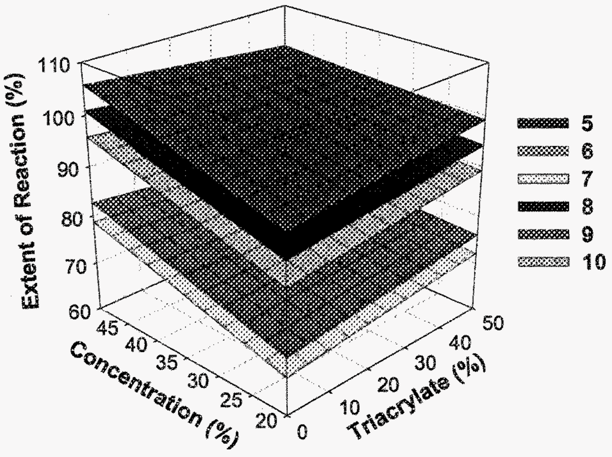


Figure 3. Graph of the response surface model of concentration of initial solution (*s*) vs. percent triacrylate (*t*) for ^{13}C NMR (extent of reaction) data. Surfaces represent fixed number of passes ($p = 35$) and formulated molecular weight ($f = 200,000$ g/mol). The surface for *bis*-(*o*-methylphenyl ketone) **6** is not seen because it falls directly below that for **5**.

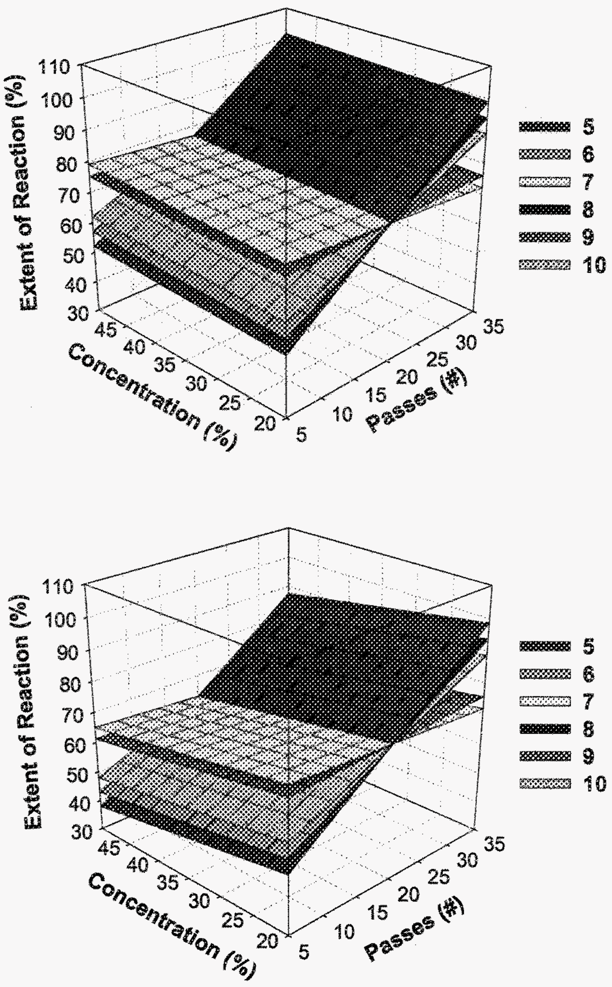


Figure 4. Graphs of the response surface model of concentration of initial solution (*s*) vs. number of passes (*p*) under the UV lamp for ^{13}C NMR (extent of reaction) data. Surfaces represent fixed formulated molecular weight (*f*) and percent triacrylate (*t*) values of (top) *f* = 200,000 g/mol and *t* = 50% and (bottom) *f* = 40,000 g/mol and *t* = 50%.

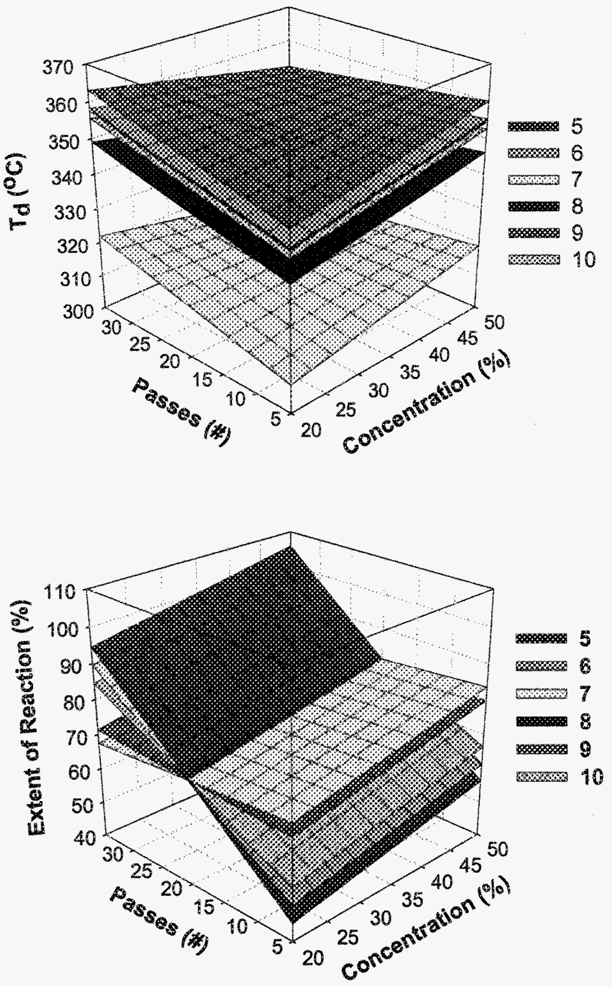


Figure 5. (top) Graph of the response surface model of number of passes (*p*) vs. concentration of the initial solution (*s*) for T_d data. (bottom) Graph of the response surface model of concentration of initial solution (*s*) vs. number of passes (*p*) for ^{13}C NMR (extent of reaction) data. All surfaces represent fixed percent triacrylate (*t* = 0%) and formulated molecular weight (*f* = 200,000 g/mol). The *bis*-(*o*-methylphenyl ketone) **8** in the lower model, although difficult to visualize, lies between **6** and **10**.

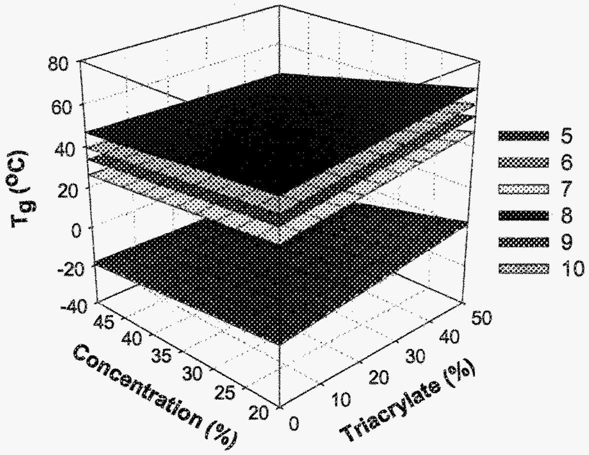


Figure 6. Graph of the response surface model of concentration of initial solution (s) vs. percent triacrylate (t) for T_g data. Surfaces represent fixed number of passes ($p = 35$) and formulated molecular weight ($f = 200{,}000$ g/mol). In this case, the *bis*-(*o*-methylphenyl ketone) **6** surface is just below that for **5**.

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(6) Although previously reported, the synthesis of **5** is presented here with additional characterization. For details, see: Ilhan, F.; Tyson, D. S.; Meador, M. A. *Chem. Mater.* **2004**, *16(16)*, 2978-80.

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(8) Due to limited quantities of the *bis*-(*o*-methylphenyl ketone)s and the fundamental nature (i.e. proof-of-concept approach) of the experimental design, our objective was to minimize the number of runs while maintaining statistical significance.

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