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EVALUATION OF TERTIARY AMINE CO-INTIATORS USING DIFFERENTIAL SCANNING PHOTOCALORIMETRY

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Key Words: Co-initiators, Tertiary Aromatic Amines, Differential Photocalorimetry, Methacrylates

ABSTRACT

The purpose of this investigation was to compare the degree of photo- and thermal-polymerization obtained using various tertiary amine co-initiators of differing reactivities and molar concentrations, utilizing differential scanning photocalorimetry (DPC) and DSC. Amines tested were 2-(dimethylamino)ethyl methacrylate (A), triethanolamine (B), N,N,3,5-tetramethyl-aniline (C), ethyl 4-dimethylaminobenzoate (D), 0.95 (A) and 0.05 (D) in combined mixture (E), 4-N,N-(dimethylamino)phenylacetic acid (F) and a newly-synthesized tertiary aromatic amine methacryloxyethyl substituted 4-N,N-(dimethylamino)phenylacetamide (G). The monomer system consisted of Bis-GMA and triethylene glycol dimethacrylate neat resins, and 0.5% camphoroquinone for all groups tested. Samples of the blended monomers with 0.5-4.0 mol/eq (co-initiator to initiator) were irradiated with visible light under N_2. The heat of reaction

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(ΔH) was calculated for each run in order to determine the degree of polymerization (DP). D resulted in a significantly higher degree of photopolymerization than A or B ($p<0.05$). No significant differences were noted between C, E, F and G ($\alpha= 0.05$). ΔH values for DSC correlated well with those of DPC. DPC appears to be an efficient tool in the evaluation of photo-initiated free radical polymerized systems.

INTRODUCTION

Previous studies have used differential scanning calorimetry to determine the degree of vinyl polymerization of thermally-cured mono-and multifunctional acrylate and methacrylate monomers [1-3]. Differential photocalorimetry (DPC) is a relatively new and powerful tool for the evaluation and characterization of photopolymerizable materials [3-6]. Photo, as well as chemical free radical polymerization of methacrylate systems is based on the "conversion" or free radical propagation of methacrylate monomers into a cured polymer network. The heat of reaction (ΔH, enthalpy) liberated during polymerization is directly proportional to the number of vinyl groups undergoing reaction within the methacrylate monomer system [1, 2]. The physical and mechanical properties of methacrylate based dental materials are strongly related to the chemical composition of the methacrylate monomers as well as their degree of polymerization to a polymer network [1]. In this preliminary investigation, the heat of reaction (ΔH) during photo-polymerization of a conventional Bis-GMA based dental methacrylate system was monitored using a differential photocalorimeter (DPC) and DSC. From the recorded heat of reaction (ΔH) the degree of vinyl double bond polymerization (DP) was calculated. The objective of this investigation was to compare the degree of photo-polymerization obtained using various tertiary aromatic and alipathic amine co-initiators of differing reactivities and molar concentrations in a Bis-GMA/triethylene glycol dimethacrylate resin system.

EXPERIMENTAL

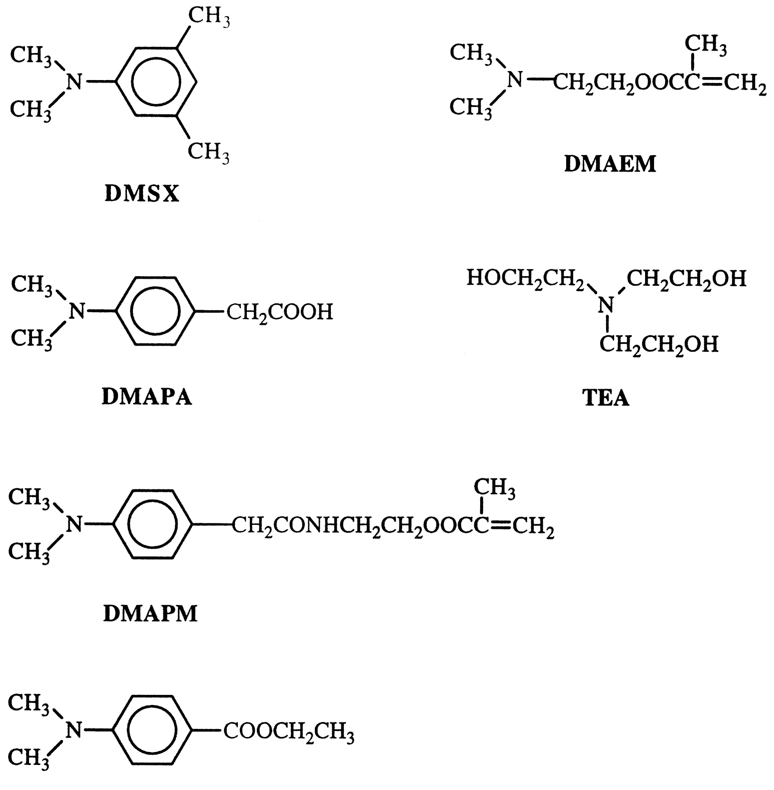
Materials

Six tertiary amine co-initiators were evaluated (Table 1 and Figure 1): four aromatic (DMSX, DMABE, DMAPA, and DMAPM) and two aliphatic

TABLE 1. Tertiary Aliphatic and Aromatic Amine Coinitiators

	CODE	MW	MP/BP(C°)
Aliphatic			
2-(dimethylamino)ethyl methacrylate	DMAEM	157	BP=182-192°
Triethanolamine	TEA	149	BP=190-193°
Aromatic			
N,N,3,5-tetramethylaniline	DMSX	149	BP=226°
Ethyl 4-dimethylaminobenzoic acid	DMABE	193	MP=64-66° at 3.5 mm
4-N,N-(dimethylamino)phenylacetic acid	DMAPA	179	MP=110-112°
Methacryloxyethyl substituted (dimethylamino)phenylacetamide *(synthesized)*	DMAPM	290	--
Combination			
DMAEM (0.95) + DMABE (0.05)	DMDM	--	--

(DMAEM and TEA) tertiary amines. DMDM, which was a combination of DMAEM (0.95) and DMABE (0.05) was also evaluated. DMSX and TEA were purified by distillation under reduced pressure and then stored in darkness under N^2. DMABE was recrystallized from an ethanol-water mixture and then dried at 60°C under vacuum in the presence of phosphorous pentoxide. DMAPA was recrystallized from water and dried at 60°C under vacuum in the presence of phosphorous pentoxide. DMAEM, camphoroquinone, triethylene glycol dimethacrylate, butylated hydroxytoluene (BHT) and 2-isocyanatoethyl methacrylate (IEM) and 2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)-phenyl] propane (BisGMA) (Figure 2) were received and utilized without further purification. All commercially-available materials were from Aldrich except IEM and BisGMA which were from Monomer-Polymer. The methacrylate monomer system used in this study is quite similar to those of commercial dental composites comprising a blended mixture of Bis-GMA and triethylene glycol dimethacrylate (70/30 w/w), camphoroquinone photoinitiator (0.5%) and BHT inhibitor at 350 ppm. Formulations of the blended methacrylate monomer system combined with varying molar concentrations 0.5-4.0 mol/eq (tertiary amine to camphoroquinone) were prepared and maintained in darkness at 23°±2°C for seven days prior to testing to enhance amine solubility. Isothermal samples (10-12 mg) of each monomer formulation (n=3) were placed in open hermetic aluminum pans



DMSX

DMAEM

DMAPA

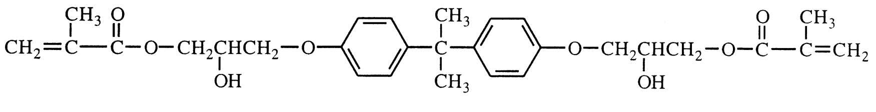
TEA

DMAPM

DMABE

Figure 1. Chemical structures of tertiary aromatic and aliphatic amines.

in the temperature controlled DPC unit and photo-irradiated with visible cold light utilizing a Xenon lamp (400-650 nm) for 20 seconds under a nitrogen atmosphere. All samples were purged with nitrogen for 2 minutes prior to irradiation in order to reduce residual oxygen. The heat of reaction ΔH (enthalpy) is directly related to the number of reaction sites (methacrylate functionality) in



BisGMA

Figure 2. Chemical structure of BisGMA resin used in many commercial dental resins.

each sample of formulation. Assuming 100% polymerization, the theoretical heat of reaction was calculated and compared to the observed heat of reaction during testing in order to determine the degree of polymerization. In order to correlate data obtained from DPC with DSC, additional samples (n=3) were made with a 3 mol/eq co-initiator to initiator ratio and photo-irradiated under nitrogen for 60 seconds. An analysis of variance procedure (ANOVA), along with a subsequent Ryan-Einot-Gabriel-Welsh (REGW) Multiple Comparison Test, were performed on all data.

Measurements

The IR spectra of the synthesized co-initiator was recorded on a MIDAC FT-IR spectrophotometer (MIDAC Corp., Costa Mesa, CA), where the sample film was placed on a NaCl crystal. ^{1}H and ^{13}C-NMR spectra were obtained on a Bruker AM 250 MHz NMR analyzer using $CDCl_3$ as a solvent at room temperature and tetramethylsilane (TMS) as the internal reference. DPC was performed on a TA Instruments differential photocalorimeter (DPC), Model 930, (TA Company, Wilmington, DE), with a 150 watt xenon lamp. DSC was carried out on a TA Instruments 910 Differential Scanning Calorimeter and Thermomechanical Analyzer (TA Instruments, TMA 2940). A scanning rate of 10°C/min was utilized under a nitrogen atmosphere. Data was analyzed by a TA Thermal Analysis 2100 program. Mass spectroscopy was performed utilizing a PE Sci Ex API 300 mass spectrometer. Methyl alcohol and water were used as the gradient. Melting points were determined using an Electrothermal melting point apparatus

Synthesis of DMAPM

Synthesis of DMAPM was performed according to the scheme presented in Figure 3. A 250 ml three-necked round bottom flask equipped with a magnetic stirrer, thermometer, condenser, and addition funnel was charged with 4-(dimethylamino) phenylacetic acid (15 g, 83.7 mmol), dibutyltin dilaurate (DBTDL) (0.05 g, 0.08 mmol) in 50g dry THF, and allowed to dissolve while mixing at 23°C. A solution of 2-isocyanatoethyl methacrylate (11.7 g, 75.3 mmol) in 20 g dry THF was then added dropwise and stirred over a period of 1 hour so that the reaction mixture did not exceed 40°C. The mixture was then allowed to mix for three hours at 45-50°C and an additional 2 hours at room temperature. The reaction was monitored with FT-IR until the NCO absorption peak at 2350 cm^{-1} was essentially absent. After evaporation of the solvent the residue

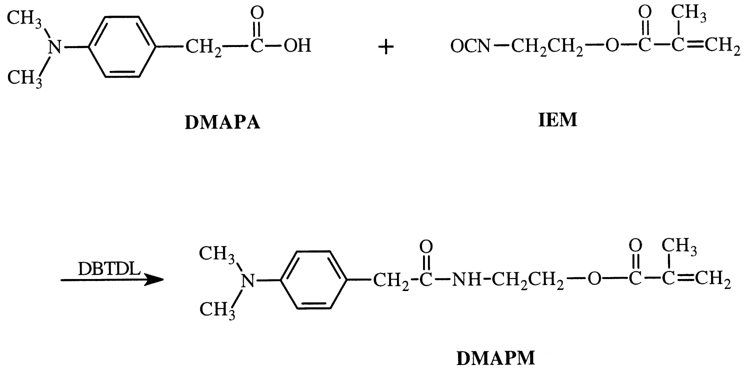


Figure 3. Synthesis of DMAPM co-initiator.

was then triturated with ethyl acetate, washed with 3% NaOH, a NaCl solution, neutralized with dilute HCl, and finally washed with water in order to remove excess DMAPA, inhibitor and catalyst. The organic layer was then dried over Na_2SO_4 and 150 ppm BHT was added. It was found that addition of this small amount of inhibitor was necessary in order to prevent premature polymerization. Solvent was removed with rotary evaporation and further stripped under vacuum at room temperature for 24 hours. The amber colored reaction product was then stored at 0-4°C in darkness under N_2. Yield 35%; Anal. calculated $C_{16}H_{22}N_2O_3$ (290.36): C, 66.19%; N, 9.64%; H, 7.64%. Found: C, 66.41%; N, 9.64%; H, 7.53%. IR (cm^{-1}) (liquid): 3370 (N-H), 2955 (CH_2), 1717 (COO^-), 1650 (NHCO), 1634 (C=C), 1617; ^{1}H-NMR (250 MH_2, $CDCl_3$): δ (ppm) = 1.92; (CH_2N), 5.56 ($C{=}CH_2$), 6.7-7.2 (aromatic); 7.7-7.9 (NHCO); ^{13}C-NMR (250 MH_2, $CDCl_3$): δ (ppm) = 18.38, 40.87 (CH_3); 39.66, 64.16, 176.74 (CH_2); 158.76, 167.69 (**C**=O); 113.12, 126.28, 130.11, 149.91 (aromatic); LC MS (291.4).

RESULTS AND DISCUSSION

The results of the ANOVA ($p<0.001$) and the REGW Multiple Range Test ($p<0.05$) indicated significant differences between the mean ΔH values of several of the tertiary amines tested (Figure 4). The calculated degree of methacrylate polymerization for each of the tertiary amine co-initiators is shown in Figure 5. DMABE resulted in a significantly higher heat of polymerization (ΔH) and degree of polymerization than DMAEM or TEA. Although DM/DM

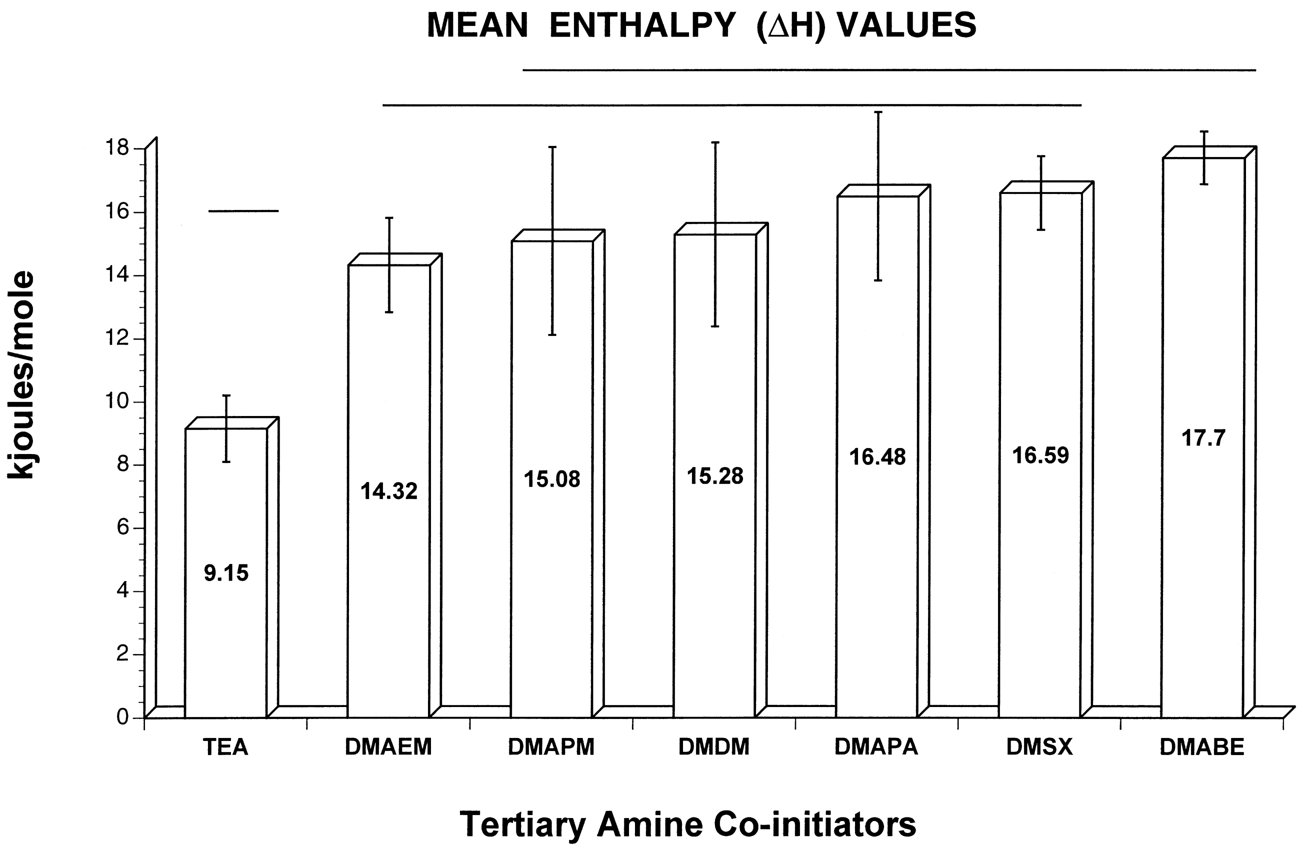


Figure 4. Mean enthalpy (ΔH) in kjoules/mole of methacrylate functionality with standard deviations. Horizontal lines denote no significant difference ($\alpha = 0.05$).

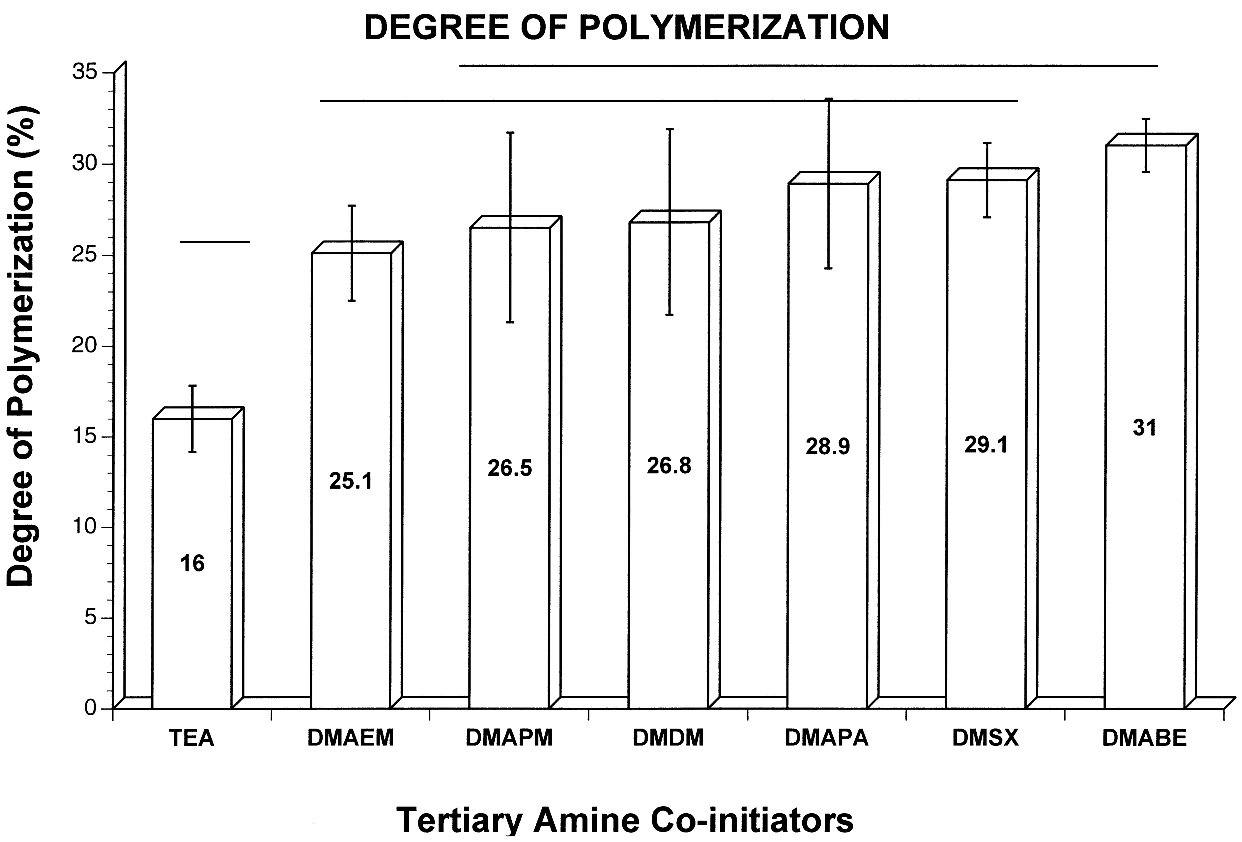


Figure 5. Degrees of polymerization (%) according to tertiary amine co-initiator utilized. Horizontal lines denote no significant difference ($\alpha = 0.05$).

resulted in a higher mean ΔH than that of DMAEM there was no statistically significant difference between the formulations ($\alpha = 0.05$). The aromatic tertiary amine co-initiators demonstrates significantly greater ΔH and degrees of conversion than the aliphatic amines TEA and DMAEM. No significant differences were noted between the newly synthesized tertiary aromatic amine DMAPM and any of the other aromatic tertiary amines ($\alpha = 0.05$).

Photo-initiated free radical polymerization utilizing tertiary aromatic amine co-initiators and diketone initiators (e.g., camphoroquinone) proceeds through a complex mechanism which is quite different from that of the chemically cured peroxide/tertiary amine systems [3, 7, 8]. Electron, and then proton (H^+) abstraction from the tertiary aromatic amine to the camphoroquinone molecule during photo-irradiation at wavelengths which the camphoroquinone primarily absorbs (>400nm) results in a *methylene-tertiary amine* initiating free radical (Figure 6) [3-5]. This effect can be attributed to a shortening of the bond distance (Figure 7) between the carbon radical and nitrogen (C_1-N) as well as nitrogen and aromatic ring (N- C_{Ar}) [3]. This is in contrast to the chemically cured methacrylate systems where amine accelerated peroxide decomposition (e.g., benzoyl peroxide) results in a benzoate radical becoming the initiating species [7, 8]. The aliphatic tertiary amine TEA resulted in a significantly lower mean ΔH value and degree of methacrylate polymerization (DP) than any of the tertiary aromatic amines tested. This is in agreement with previous investigations which have shown aromatic amines to have considerably higher radical

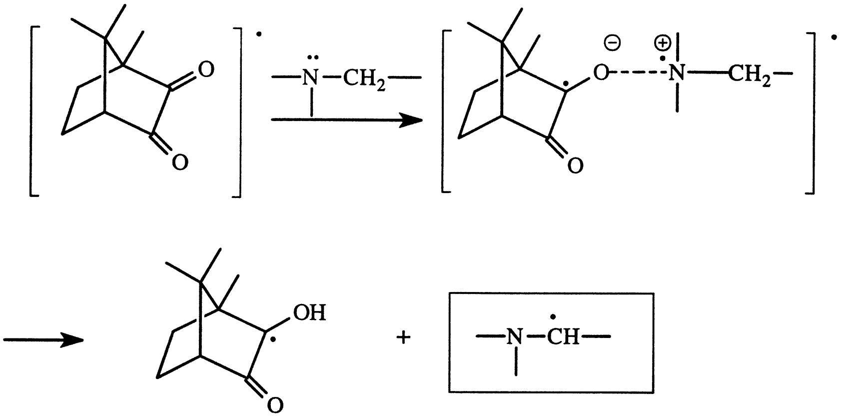


Figure 6. Photo-reduction behavior of camphoroquinone in the presence of amine co-initiators. Adapted from Mateo, *Macromolecules*, 27, 7795 (1994).

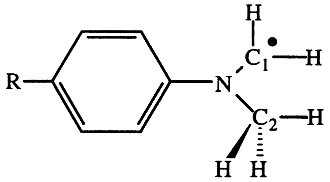


Figure 7. Geometric parameters of initiation radical. Adapted from Mateo, *Macromolecules*, 27, 7797 (1994).

efficiency than that found with aliphatic amines [3-5]. However, no significant difference was noted between the DP of the aliphatic amine DMAEM and several of the tertiary aromatic amines. This may be due in part to the low molecular weight and high solubility of this methacrylate substituted co-initiator in a methacrylate based system. The high ΔH and DP of DMABE is most likely attributed to the electron withdrawing character of the ethyl ester *para* substituent as well as its increased solubility. High molecular weight, hydrogen bonding, and low solubility, which would result in decreased diffusion and mobility in addition to the character of the *para* substituents, may explain the low ΔH and DP of DMAPA and DMAPM when compared to DMSX and DMABE. A 20 second photo-irradiation time was chosen to simulate the absolute minimum recommended exposure time for many commercial dental light-cure methacrylate systems. However, the lower than clinical light intensity of the DPC unit and short exposure time may have resulted in less than expected degrees of polymerization than those previously reported for commercial dental composites. Table 2 shows the DPC combined mean enthalpy values of all

TABLE 2. DPC Combined Mean Enthalpy Values with Standard Deviations in Kjoules/Mole of Methacrylate Functionality According to Mol/Eq of Amine to Camphoroquinone. Values with the Same Letter Denote no Significant Difference ($\alpha = 0.05$).

Mol/eq	Mean Enthalpy
0.5	12.11 (2.847) A
1	15.88 (2.94) B
2	15.67 (3.54) B
3	16.02 (2.67) B
4	15.03 (3.15) B

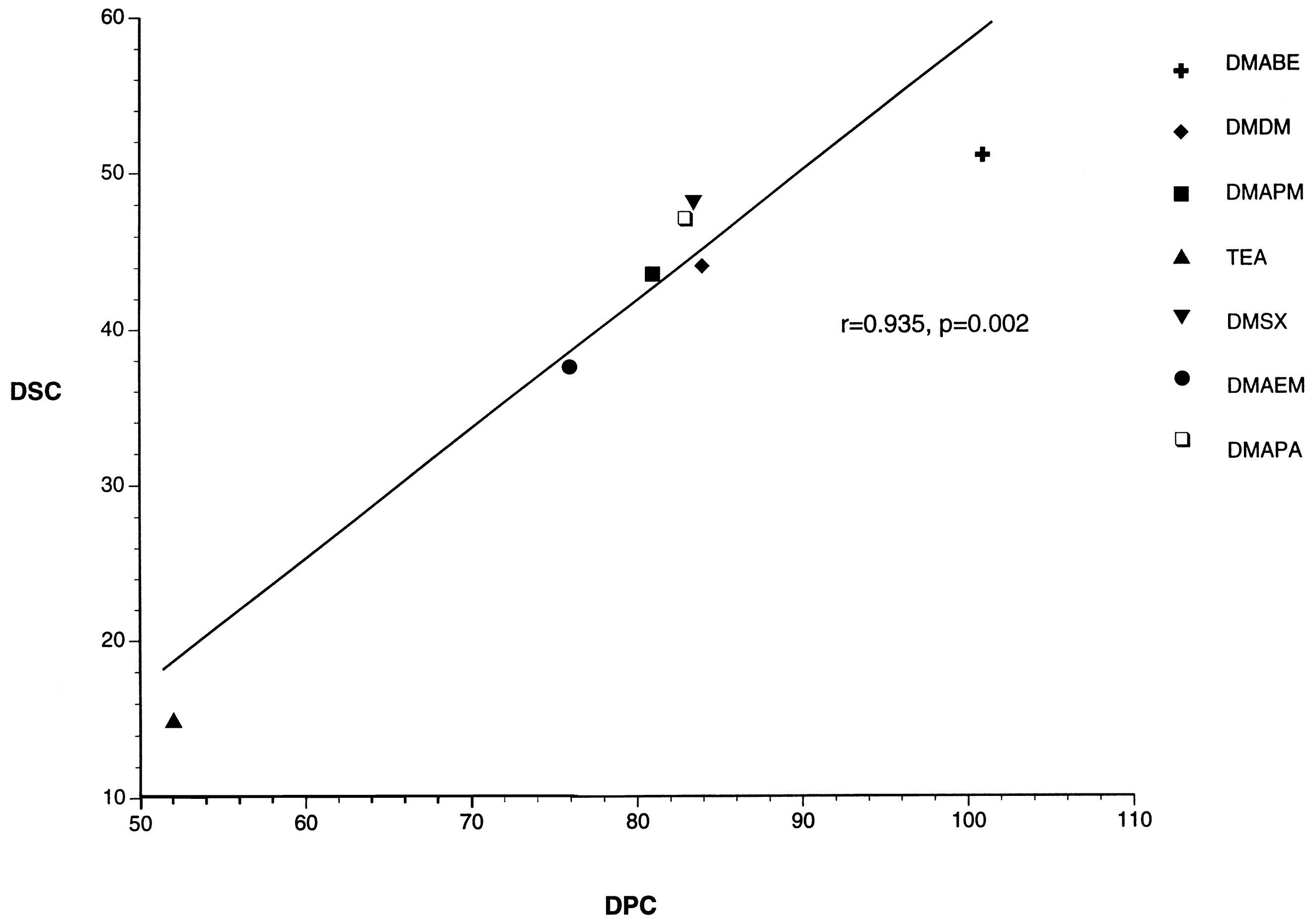


Figure 8. Correlation plot of co-initiator DSC and DPC ΔH values in kjoules/mole of methacrylate functionality.

amines tested according to mol/eq of amine to camphoroquinone. A ratio of 0.5 mol/eq co-initiator (amine) to initiator resulted in a significantly lower DP than the other ratios tested. Although no significant differences were noted between the degree of polymerization obtained with 1.0-4.0 mol/eq ratios, higher values of DP were obtained with a 3 mol/eq of amine to camphoroquinone. In order to correlate the data between DPC and DSC additional samples were prepared and run with a 3.0 mol/eq amine-to-camphoroquinone ratio. ΔH values for DSC correlated well ($r=0.935$) with those of DPC (Figure 8). DPC appears to be an efficient tool in the evaluation of photo-initiated free radical polymerized systems.

CONCLUSION

The degree of photo and thermal-polymerization obtained using various tertiary amine co-initiators of differing reactivities and molar concentrations was determined by differential photocalorimetry (DPC) and DSC. Tertiary aliphatic amines generally resulted in lower degrees of polymerization than aromatic amines. Electron withdrawing substituants attached at the *para*-position of the aryl group with respect to the nitrogen atom on the aromatic amine initiating radicals tended to increase their relative reactivity toward methacrylate polymerization. DPC appears to be an efficient tool in the evaluation of photo-initiated free radical polymerized systems.

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