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SYNTHESIS AND CHARACTERISATION OF URETHANE - METHACRYLATES I.

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The paper describes the synthesis of urethane methacrylate resins by reaction of tolylene diisocyanate (TDI), butanol-1 (B) and 2-hydroxyethylmethacrylate (HEMA) by a two step procedure. Characterisation was done using FT-IR, FT-NMR, Mass Spectroscopy. The effect of temperature on the UV-curing behaviour was investigated by differential photocalorimetry. An activation energy of 8.4 kJ/mole was found in the temperature range of 50-100°C. Free radical polymerisation in presence of benzoyl peroxide was also investigated. The polymers were stable upto 200°C in N_2 atmosphere. A two step decomposition was observed in the temperature range of 200-500°C.

Considerable research work has been expended in the past for development of radiation sensitive polyurethane oligomers end-capped with acrylate or methacrylate moieties [1, 2]. These oligomers are normally prepared by a two step procedure by reacting aromatic diisocyanates such as tolylene diisocyanate (TDI), xylidine diisocyanate, isophorone diisocyanate with a polyether or polyester macroglycol followed by end-capping with 2-hydroxyethylacrylate or 2-hydroxyethylmethacrylate (HEMA). The effect of oligomer type, molecular weight and reactive diluent on the properties of urethane acrylates is also well documented in literature [3-6]. However, no studies have been reported on the curing behaviour of urethane-methacrylate monomers, which can be prepared by reacting HEMA and alcohol with diisocyanate. It was, therefore, considered of interest to study the polymerisation of methacrylates having pendant urethane linkages.

Such monomers can be prepared from diisocyanates such as TDI by following two step reaction scheme.

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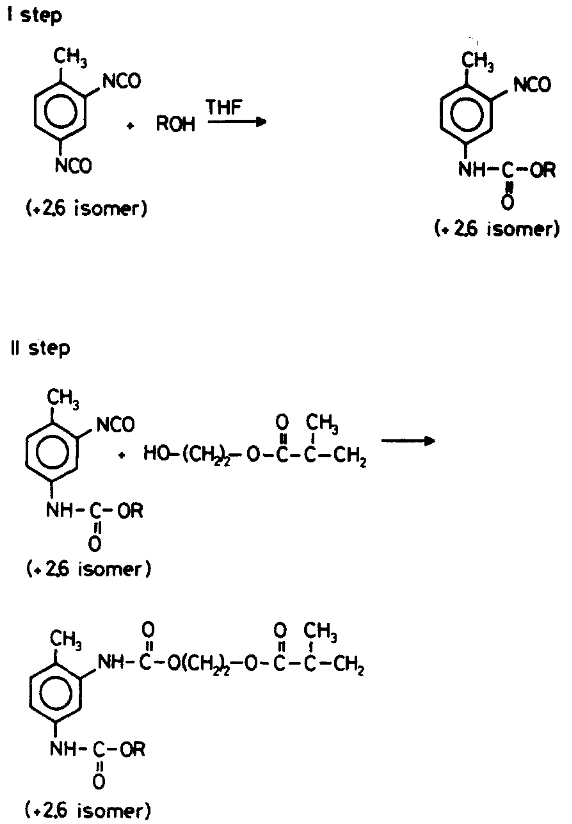


Reaction scheme for synthesis of urethane-methacrylate monomers

The isocyanate group at 4-position in 2,4-TDI is believed to be more reactive [7]. Therefore, by changing the sequence of addition of ROH and HEMA, the proportion of methacrylate moiety can be changed at 2- or 4-position. In the present work n-butanol (B) was used for the urethane methacrylate monomer preparation.

Experimental

Materials

A 80:20 mixture of 2,4-tolylene diisocyanate with 2,6-tolylene diisocyanate (TDI), 2-hydroxyethyl methacrylate (HEMA) (Fluka) and stannous octoate were used as received. Tetrahydrofuran (THF) (E. Merck) was dried by passing sodium wire and then distilled. 1-Butanol (B) (S. D. Finechem.) was refluxed with freshly ignited calcium oxide for four hours. The alcohol was decanted from lime, refluxed with magnesium turnings and then distilled. Benzoyl peroxide (Bz_2O_2) (Loba-Chemie) was recrystallised from chloroform.

Preparation of urethane-methacrylate monomer

The reaction was carried out in dark at room temperature (30±2°) in a 100 ml round bottom flask having a calcium chloride guard tube. Few drops of stannous octoate (catalyst) and 10 ml of THF were placed in the flask. HEMA (0.04 mole) was then added and solution was stirred using a magnetic stirrer. TDI (0.04 mol) was then added and reaction was carried out for four hours. Then, 1-butanol (0.04 mol) (*B*) and few more drops of stannous octoate were added to the above reaction mixture and the reaction was carried out at room temperature (30±2°). The reaction was monitored by following the disappearance of isocyanate peak (2270 cm^{-1}). The monomer thus obtained has been designated as THB. The sequence of addition of HEMA and B was then reversed. All other conditions were kept same. The resultant product has been designated as TBH.

Polymerisation

The polymerisation was carried out in nitrogen/air atmosphere by using thermal and photochemical means. A DuPont 2100 thermal analyser having a 930 DPC module was used for monitoring the photochemical polymerisation. For this purpose 5 mg of monomer samples were micropipetted into tared DSC pan. All the measurements were done isothermally. The monomer samples in DSC pan was equilibrated at the desired temperature (40-100°) for 3 min. Then the shutter of DPC was opened for 6-10 min to expose the sample. The duration of exposure depended on the temperature of polymerisation.

THB and TBH polymerisation was also done thermally at a programmed rate of heating using Bz_2O_2 (1%, 2% and 3%) as initiator. Bz_2O_2 in THF solution was added to the monomer and mixed well. Then the solvent THF was removed using a vacuum pump. A DuPont 9900 thermal analyser having a 910 DSC module was used to follow polymerisation. A sample size of 17±3 mg and heating rate of 10 deg/min was used.

Polymerisation using free radical initiator was also done in solution. For this purpose, 2 g of monomer was dissolved in 20 ml of THF and 1% of Bz_2O_2 was added. Polymerisation was carried at 60° in N_2 atmosphere for 5 h 30 min and polymer was removed by precipitation.

Characterisation

A Digilab FTS-40 FT-IR spectrophotometer was used for recording ir spectra of samples as thin films or in KBr pellets. Structural determination was done by recording the ^{1}H-NMR spectra at room temperature using DMSO-d_6 as solvent, tetramethyl silane as internal standard and a Jeol-JNM-FX 100 FT-NMR spectrometer. The conditions were: field strength 99.55 MHz and spectral width 1500 Hz. A Jeol-JMS-DX300 mass spectrometer was used to record mass spectra. An ionisation potential of 70 eV was used.

Thermal stability of polymers was evaluated by using a DuPont 1090 thermal analyser having a 951 TG module. A heating rate of 10 deg/min and 10±2 mg of polymer sample was used. TG traces were recorded in N_2 atmosphere in the temperature range of 50° to 600°.

Results and discussion

The isocyanate group present in the 4-position of TDI is more reactive due to (–I) effect of –NCO group at 2-position. Therefore, when HEMA or butanol is added in the first stage, it is expected, that the reaction will take place mainly with the 4-NCO group. However, since the TDI was a mixture of 2,4- and 2,6-diisocyanates, therefore TBH of THB will also have 2,6-product along with the expected major product i.e. 2,4-derivative. The only difference between TBH and THB monomers is a difference in distribution of methacrylate group at 4-position. In TBH the relative proportion of methacrylate group at 4-position is low whereas in THB it will be higher. This difference arises due to different sequence of addition of HEMA to TDI.

Addition of HEMA or butanol for preparation of TBH or THB respectively in the second step was monitored by FT-IR. Considerable reduction in the intensity of absorption band at 2270 cm^{-1} was observed after 15 min of the reaction (Fig. 1). The reaction was continued till this peak disappeared completely (approximately 3-4 h).

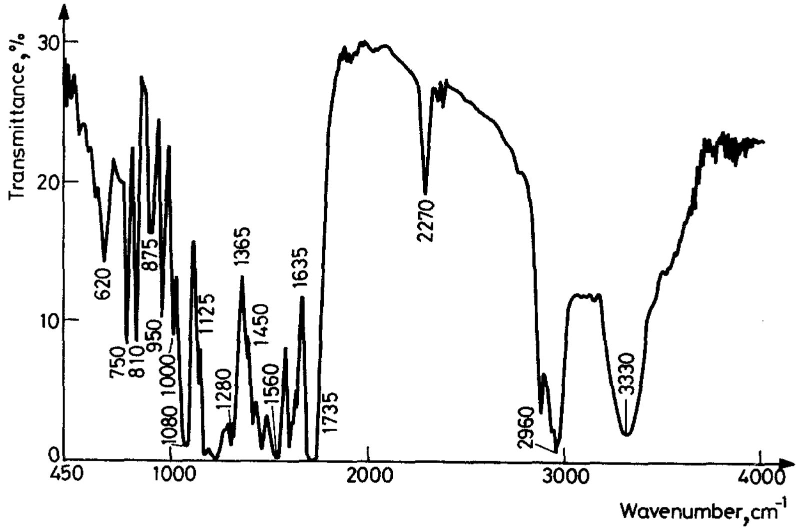
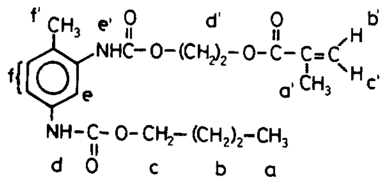


Fig. 1 FT-IR spectrum of reaction product of TDI, HEMA after 15 min of addition of butanol

In the IR spectra of monomers, the characteristic carbonyl stretching of urethane linkage was observed at 1735 cm^{-1}. The absorptions resulting from N-H stretching and bending vibrations were observed at 3330 cm^{-1} and 1560 cm^{-1} respectively. The C–H stretching and bending vibrations were at 2960 cm^{-1}, 1480 cm^{-1} and 1450 cm^{-1} respectively; C–O stretching vibrations were at 1330 cm^{-1}, 1280 cm^{-1} and 1080 cm^{-1}. The double bond of acrylate moiety was observed as a medium intensity peak at 1635 cm^{-1}. The aromatic C–H bending vibrations were at 875 cm^{-1} and 810 cm^{-1}. The absorption caused by C–N was at 1235 cm^{-1} (Fig. 2).

In the IR spectrum of polymer (Fig. 2), the peak at 1635 cm^{-1} was not observed. This is because of the conversion of C=C to C–C. No absorption peak was observed around 1660 cm^{-1} in monomer and polymer thereby indicating the absence of urea linkage.

In the ^{1}H-NMR spectra of monomers, 12 sets of equivalent protons are present in THB/TBH which resonate at different field strengths due to their different environments. The methyl protons (*a*) of alcohol side chain appear at 0.911 ppm (triplet, 3H), two sets of methylene protons at 1.470 ppm (multiplet, 4H) and the methylene proton (*c*) which is attached to the oxygen atom at 4.051 ppm (triplet, 2H).



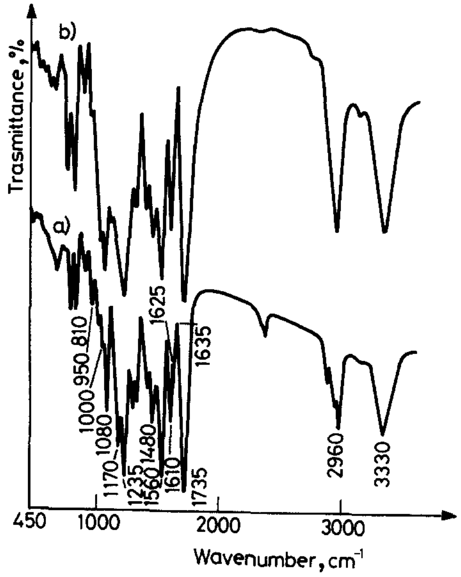


Fig. 2 FT-IR spectra of (a) THB monomer (b) THB polymer

The methyl protons (*a'*) of the methacrylate side chain appear at 1.889 ppm (singlet, 3H). A singlet was observed at 4.327 ppm (4H) and can be attributed to methylene groups at position (*d'*) of the methacrylate moiety. The two protons (*b'* and *c'*) of the methylene-end are magnetically none-quivalent, therefore, were obtained at 5.687 ppm (singlet, 1H) and 6.055 ppm (singlet, 1H). The methyl protons (*f'*) attached to the aromatic ring appear at 2.110 ppm (singlet, 3H). The aromatic protons (e and f) appear at 7.077 ppm (singlet, 2H) and 7.489 ppm (singlet, 1H). The protons (*d*) at the -NH- which is para to the methyl group appear at 9.489 ppm (broad singlet, 1H) and -NH- proton which is ortho to the methyl group appear at 8.905 ppm (broad singlet, 1H). To confirm whether there is coupling between -NH- and aromatic protons, proton decoupled NMR was also recorded. No coupling was indicated in this region. Therefore, this broad singlet may arise due to presence of 2,6-and 2,4-isomers in TBH and THB. ^{1}H-NMR spectrum of TBH is shown in Fig. 3.

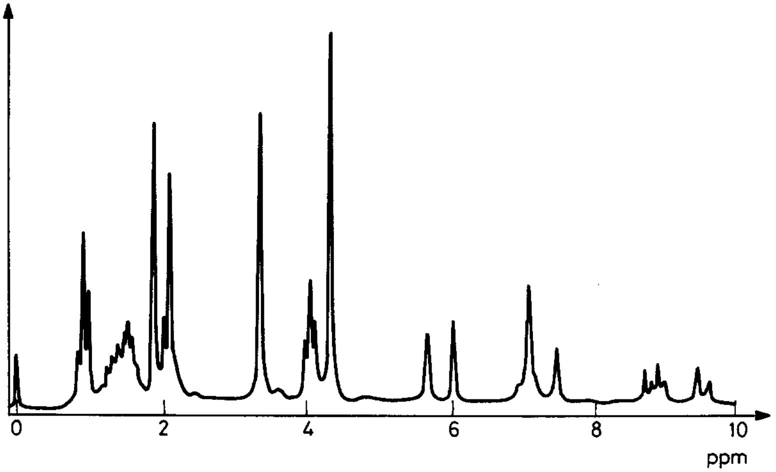


Fig. 3 ^{1}H-NMR spectrum of TBH

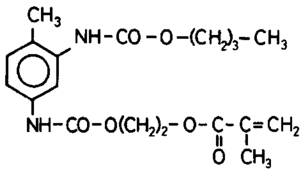
In the mass spectra of TBH and THB, molecular ion peak was observed at *m/e* 378. The other prominent peaks in TBH were at *m/e* 322, 248, 174, 166, 148, 147, 113, 69 and 57. The fragment ions at 57 and 69 can be explained by the formation of $C_4H_9^+$ and $CH_2=C(CH_3)-C^+=O$. The fragmentation pattern of THB is shown in Fig. 4.

During the photopolymerisation (DPC) of TBH and THB monomers, radicals are generated and heat is liberated due to conversion of π-bond of methacrylate moiety into σ-bonds. An exotherm was, therefore, observed in the heat flow calorimetric traces recorded during irradiation of monomers at a constant temperature (Fig. 5). The exotherm was preceded by an induction period which depended on the temperature of polymerisation and ranged from 36 sec to 64 sec. From the heat flow calorimetric trace, peak maximum time, percent of reaction at peak and enthalpy of reaction could be determined and these results are summarised in Table 1.

Table 1 Results of photopolymerisation of urethane-methacrylate monomers in air atmosphere

Sample designation	Temp., °C	Induction time, Sec	Peak max. Sec	Reacted at peak., %	Enthalpy, J/g
THB	41.4	63.2	88.4	25.9	62.3
	51.4	59.4	84.2	26.5	74.4
	61.4	53.5	74.2	28.3	56.7
		(36.7)	(48.6)	(29.5)	(78.2)
	76.4	47.0	64.6	26.7	41.7
TBH	41.4	54.6	76.4	26.1	32.4
	51.4	52.9	75.6	22.4	80.1
	61.5	(36.7)	(48.4)	(18.1)	(83.8)
	76.5	45.3	63.0	25.3	45.6
	101.6	38.9	53.4	25.8	28.4

Figures in parenthesis indicate the results obtained in N2 atmosphere



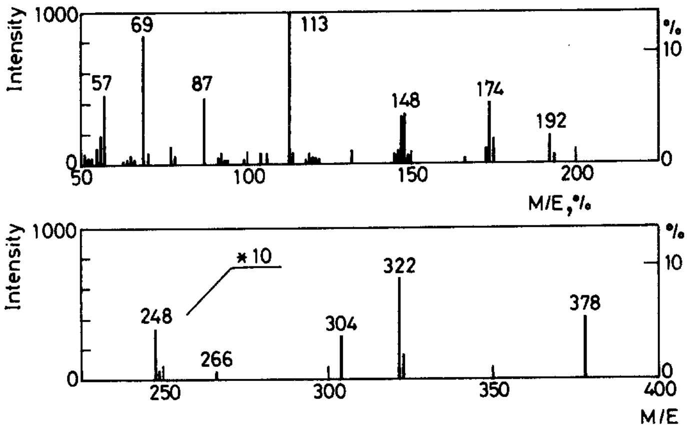


Fig. 4 Electron induced fragmentation pattern of THB (70 eV)

Photopolymerisation was carried out both in static air atmosphere as well as N_2 atmosphere. As expected, in air atmosphere the induction period, peak maximum time, is higher while the fraction reacted at peak and enthalpy is lower. This is because of the air inhibition of the photopolymerisation reaction.

The kinetic software available with the instrument was used for evaluating fractional conversion and rate of conversion. This software uses the autocatalytic rate equation

$$\frac{dc}{dt} = k(1-c)^n (c)^m$$

where k = apparent rate constant, n and m are the n^{th} order exponent and autocatalytic exponent respectively.

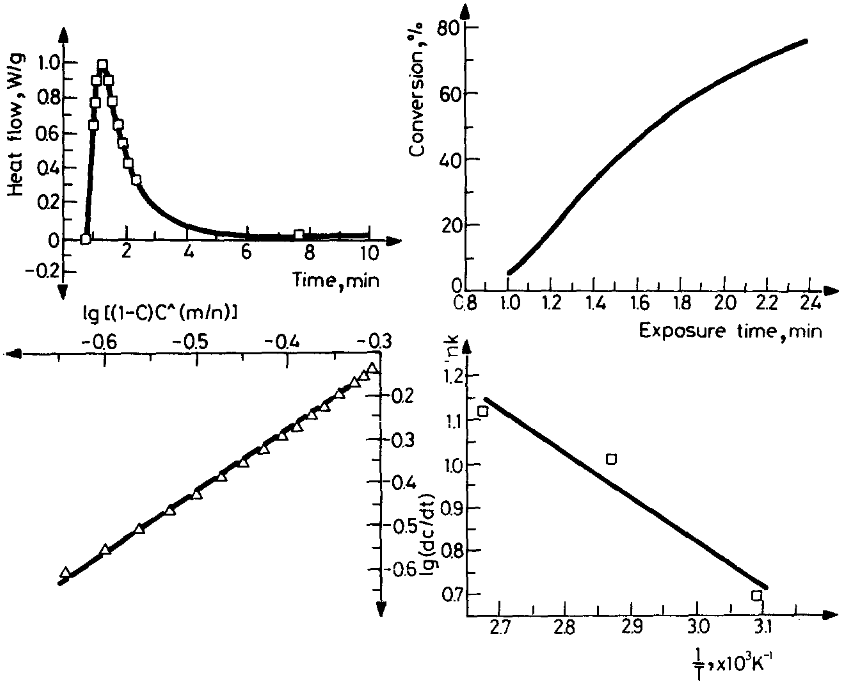


Fig. 5 Photopolymerisation of THB at 51°C

A typical plot of percent conversion *vs.* exposure time is shown in Fig. 5. From the knowledge of apparent rate of polymerisation (dc/dt), the apparent rate constant was determined by plotting log dc/dt *vs.* log[(1–c)c ^ (m/n)] (Fig. 5). The values of n, m and k in air and nitrogen atmosphere for the two monomers are given in Table 2.

Table 2 Rate constant, n and m values for photopolymerisation of urethanemethacrylate monomers in air atmosphere

Sample designation	Temp., °C	n	m	k, min^{-1}
THB	41.4	1.37	0.503	2.40
		±0.019	±0.01	±0.052
	51.4	1.28	0.478	2.31
		±0.014	±0.0079	±0.039
	61.4	1.09	0.454	2.65
		±0.008	±0.0044	±0.025
		(0.781)	(0.375)	(3.82)
		(±0.031)	(±0.017)	(±0.14)
	76.4	0.967	0.392	2.54
		±0.016	±0.009	±0.048
TBH	51.4	1.44	0.435	2.01
		±0.025	±0.014	±0.06
	61.5	(1.46)	(0.364)	(2.73)
		(±0.029)	(±0.016)	(±0.091)
	76.5	1.19	0.437	2.75
		±0.014	±0.008	±0.046
	101.6	1.10	0.4	3.07
		±0.0094	±0.0052	±0.034

Figures in parenthesis indicate the results obtained in N_2 atmosphere

The change in reaction rate as a function of temperature was used to calculate the activation energy for the photopolymerisation by using Arrhenius equation (Fig. 5). The activation energy was found to be 8.4 kJ/mole in air atmosphere for TBH.

Thermal polymerisation of THB was investigated by using different weight percentages of benzoyl peroxide (1%, 2%, 3%). Exothermic transition indicating polymerisation was observed in the temperature range of 90-140° (Fig. 6). From these exotherms, the temperature of onset (T_1), peak position (T_2) and completion (T_3) was noted down. An increase in initiator concentration resulted in a decrease in T_1, T_2 and T_3. For example, T_2 was found to be 134.94, 114.85 and 105.84° when 1, 2 or 3% benzoyl peroxide was used.

Thermal behaviour of polymers obtained by polymerisation in THF using 1% benzoyl peroxide as an initiator was investigated by dynamic thermogravimetry in nitrogen atmosphere. The polymers were stable upto 200° and started decomposing above this temperature. A two step decomposition behaviour was observed in polymers derived from THB and TBH (Fig. 6).

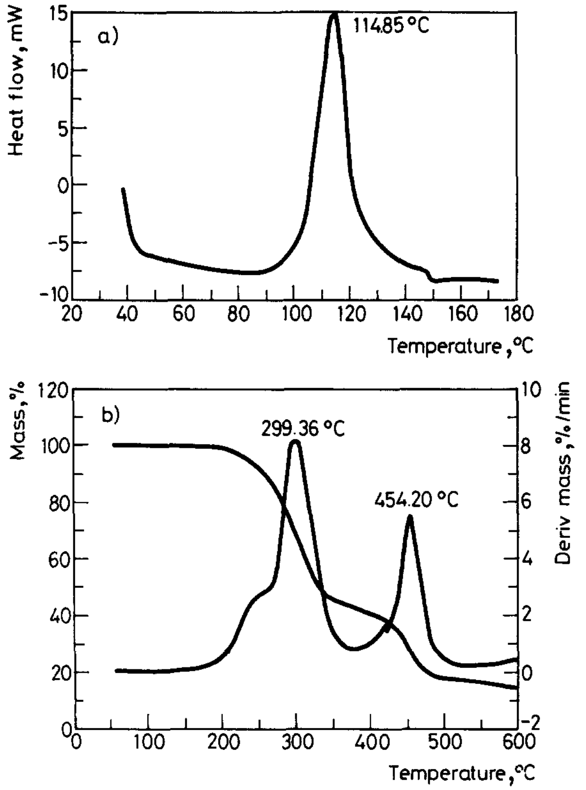


Fig 6 (a) DSC scan of THB contauning 2% benzoyl peroxide (heating rate 10 deg/min). (b) TG trace of polymer based on TBH

Comparison of photopolymerisation of THB and TBH, monomers reveals that the rate is independent of the position of methacryloyl group in the benzene ring (i.e. 2 or 4). Both the monomers polymerised with similar speeds.

* * *

The Instrument system of E. I. DuPont de Nemours & Co. is acknowledged for differential photocalorimeter studies.

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Zusammenfassung — Vorliegende Arbeit beschreibt die Synthese von Urethanmethacrylat-Harzen durch die Reaktion von Toluylendiisocyanat (TDI), Butanol-1 (B) und 2-Hydroxyethylmethacrylat (HEMA) in einem zweistufigen Herstellungsverfahren. Charakterisiert wurden die Produkte mittels FT-IR, FT-NMR und Massenspektroskopie. Anhand von Differentialfotokalorimetrie wurde der Einfluß der Temperatur auf das UV-Aushärtungsverhalten untersucht. Im Temperaturbereich 50-100°C wurde eine Aktivierungsenergie von 8.4 kJ/mol gefunden. Weiterhin wurde auch die Radikalkettenpolimerisation in Gegenwart von Benzoylperoxid untersucht. In Stickstoffatmosphäre sind die Polymere bis 200°C stabil. Im Temperaturbereich 200-500°C wurde eine zweistufige Zersetzung beobachtet.