Synthesis and Characterization of Curable Methacrylate-Based Monomers

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ABSTRACT: The synthesis of new methacrylate-based, curable macromonomers, 4,4′-bis[2-hydroxy-3-aminopropylmethacrylate] diphenyl ether (BHAPE) and 4,4′-bis[2-hydroxy-3-aminopropylmethacrylate] diphenyl methane (BHAPM), is reported. BHAPE and BHAPM were prepared by the reaction of glycidyl methacrylate (GMA) with 4,4′-diaminodiphenyl ether and 4,4′-diaminodiphenyl methane, respectively. The progress of the reaction was monitored by thin-layer chromatography (TLC), and the structure of the monomers was characterized by Fourier transform infrared (FTIR) and ^{1}H-NMR spectroscopy. Thermal curing of the monomers was conducted in a differential scanning calorimeter (DSC) with peroxide as the initiator. Thermal curing of the monomers showed the highest rate at 100°C with the activation energy value in the range 80–90 kJ distilled/mol. The water absorption properties of the cured samples in water, acidic, and basic solutions were studied. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 467–472, 2010

Key words: curing of polymers; differential scanning calorimetry (DSC); resins; synthesis

INTRODUCTION

Crosslinking monomers are synthesized to improve the mechanical and processing properties of the composite. Such composites demonstrate reduced water uptake and self-adhesion to substrates. Vinyl ester and unsaturated polyester resins typically used in making composites contain high concentrations of reactive diluents, such as styrene, to allow these resins to be molded. However, because of the volatilization of styrene, nonvolatile reactive diluents, such as methacrylate-based macromonomers, offer a large advantage over current reactive diluents. The monomer matrix systems of the composites, which are currently mostly based on a mixture of dimethacrylates, have to fulfill a number of basic requirements as far as the reactivity, stability, or toxicity of the monomers used and the properties of the formed polymer network are concerned. Informative reviews on different monomer systems are available.[1] Multifunctional monomers of low polymerization shrinkage and high degree of conversion, such as methacrylate- and acrylate-based monomers, act as crosslinking agents and, thus, crosslink the polymer chains as the film is cured, forming links between oligomer molecules and other molecules in the formulation.[2–5] Monomers of this type are able to cure very rapidly and provide low volatility, high reactivity, and good flexibility.[6] It has also been shown that the presence of pendent hydroxyl groups in dimethacrylate compounds, such as bisphenol A glycol dimethacrylate, enhances polymerization rates because it increases the viscosity of the system because of strong hydrogen bonding.[7] These polymers have acquired prime importance in various avenues of industrial applications, especially in areas such as pharmaceutical use for drug delivery,[8] pressure-sensitive adhesives,[9] dental composites,[10,11] superabsorbents,[12] industrial coatings, leather adhesives, and nonlinear optical materials.[13–15] The important factor that affects the flexibility of the polymer chain is the distance between double bonds in the crosslinker structure. In addition, final conversions are often limited by vitrification and topological factors governing steric crowding, accessibility of reactive sites, and kinetic access to pendant double bonds.[16,17] These problems can be partially overcome by the incorporation of long, flexible spacers between the vinyl groups.[18]

In this article, we report the synthesis and characterization of two multifunctional methacrylate-based macromonomers with a long distance between functional groups. The monomers were prepared by a simple one-step reaction between GMA and aromatic diamines, and the progress of the reactions was monitored by TLC. The final structure of the monomers was checked by ^{1}H-NMR and FTIR
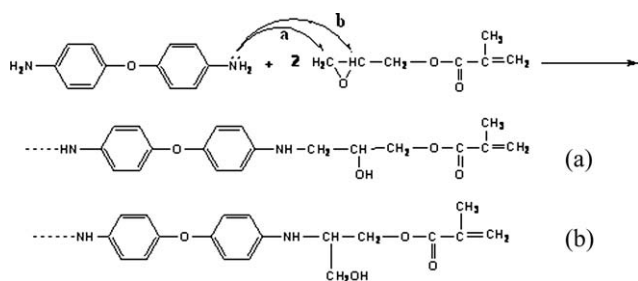
Scheme 1 Mechanism of the reaction for the synthesis of the macromonomers.

spectroscopy. Thermal polymerization of the prepared monomers to thermoset products was carried out in DSC in the presence of a free-radical initiator. The water absorption properties of the cured samples are also reported. These monomers can be used as dental restorative resins, in coatings, in composite materials, and also as low-viscosity reactive diluents in unsaturated polyester resins. Monomers of this type, with long and flexible spacers between the vinyl groups, are able to cure very rapidly and provide low volatility, high reactivity, and good flexibility.

EXPERIMENTAL

Materials

GMA (Merck, Germany) was used after its structure was analyzed by FTIR spectroscopy. 4,4′-Diaminodiphenyl ether (DDE) and 4,4′-diaminodiphenyl methane (DDM) were purchased from Merck and were used without further purification.

Measurements

The FTIR spectra were recorded on a Bruker series Vector 22 (Germany), with a thin film of a drop of monomer on the surface of an NaCl disk. ^{1}H-NMR spectra were recorded on a Bruker AQS Advance 300 MHz instrument, with $CDCl_3$ as the solvent. Thermal curing of the monomers was carried out in a PerkinElmer DSC-7 instrument (USA) at different heating rates of 5, 10, 15, and 20°C/min under an N_2 atmosphere.

Monomer synthesis

4,4′-Bis[2-hydroxy-3-aminopropylmethacrylate] diphenyl methane (BHAPM) and 4,4′-bis[2-hydroxy-3-aminopropylmethacrylate] diphenyl ether (BHAPE)

A mixture of GMA (2.0 mL, 15 mmol) and DDM (1.48 g, 7.5 mmol) or DDE (1.38 g, 7.5 mmol) with a molar ratio of 2:1 was stirred in an argon atmosphere at 110–120°C without the addition of solvent.

The progress of the reaction was monitored by TLC; this was followed by the measurement of the disappearance of the absorption peak at 915 cm^{-1}, characteristic of terminal epoxy groups. After the reaction was complete, the mixture was cooled slowly under an argon atmosphere. The monomers BHAPE and BHAPM were viscous brown and yellow, respectively. These monomers were identified by FTIR and ^{1}H-NMR spectroscopy. The reaction procedure is shown in Scheme 1.

Water absorption

Samples for the water absorption tests were prepared by the curing of a certain amount of uniform viscous liquid of BHAPE and BHAPM with 1 wt % benzoyl peroxide in an aluminum foil mold *in vacuo* at 180°C for 3 h. We chose a temperature well above the maximum curing temperature shown by DSC measurement *in vacuo* for 3 h to obtain fully cured samples. Samples with dimensions of 8×5 mm^2 with 0.7–1.2 mm thickness were cut and used for the water absorption tests. The samples were weighed and immersed in a flask containing water at room temperature. After a certain time, the exposed samples were dried with a soft tissue before they were weighed. Three samples were used for the measurement of water absorption, and the reported value is the average of the three readings. Also, the same curing procedure was used to prepare samples for the absorption tests in 30% acid and 50% base solutions.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

GMA monomer, containing methacrylic and epoxy groups, offers a dual functionality and enters into a vast number of chemical reactions by opening their oxirane ring[19,20] and by copolymerization with other vinyl monomers,[21–24] thus offering an excellent
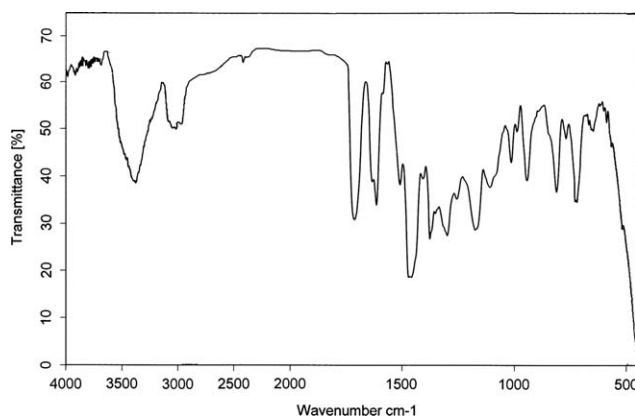
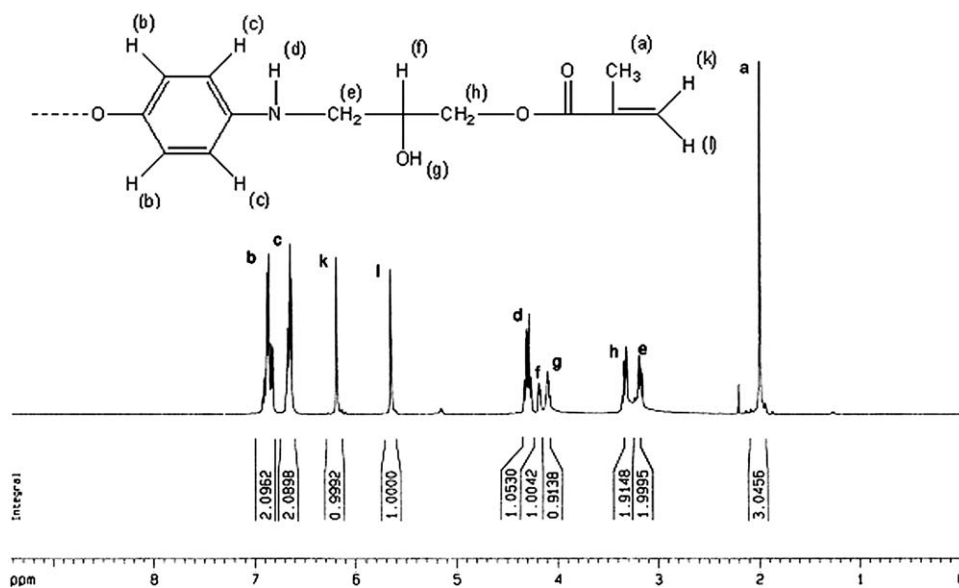
Figure 1 FTIR spectrum of BHAPM.

Figure 2 ^{1}H-NMR spectrum of BHAPE.

opportunity for chemical modification. The epoxy group of GMA enables reactions with compounds containing active hydrogen, such as amines, carboxylic acids, and phenols. The viscous products obtained from the reaction of the epoxy group of GMA with the amine groups of DDE and DDM were very sensitive to the air presence at the high temperature; this led to a hard, insoluble product, probably by undesirable polymerization through olefinic double bonds. Therefore, to measure the end of the reaction, separate reactions were carried out for different periods of time. The reaction mixtures were cooled to room temperature under an argon atmosphere before they were exposed to the air. We determined the time required to complete the reaction by monitoring the TLC of the reaction mixture. This confirmed that the reactions for the synthesis of BHAPE and BHAPM were completed after almost 45 min. The important absorption peaks observed in the FTIR spectra of both monomers of BHAPM and BHAPE [at (cm^{-1}) 1719 (C=O), 1636 and 950 (stretching and bending vibrations of the —C=CH$_2$), 1470 (C=C aromatic), and 3600–3380 (—O—H and —N—H stretching vibrations), as shown in Figure 1 for BHAPM] were indications of the proposed structure for the monomers. With a difunctional reagent such as DDE, there is the possibility of two isomers being formed, which is shown in Scheme 1 for BHAPE, although it was not a feasible proposition to attempt to separate these isomers. The ^{1}H-NMR
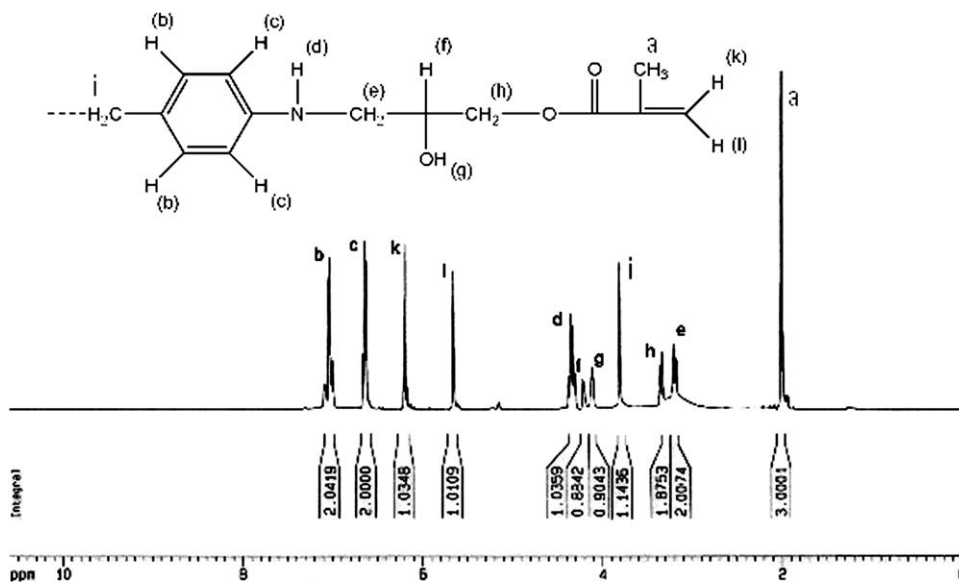

Figure 3 ^{1}H-NMR spectrum of BHAPM.

spectra of these monomers obtained from a number of reactions indicated that the major product was the linear isomer, as shown in Scheme 1(a). The ^{1}H-NMR spectra of the monomers are shown in Figures 2 and 3, and the major signals have been assigned. The protons of the methyl group of methacrylate, hydroxyl group, and secondary amine —NH— appeared at 2.0, 4.1, and 4.32 ppm, respectively. The signals for vinyl protons at 5.65 and 6.25 ppm and aromatic protons at 6.70 and 6.95 ppm and the signal of methylene protons for the BHAPM compound at 3.80 ppm all confirmed the proposed structures.

Thermal curing

The study of the relationship between the polymer formed and the network properties generated during the cure reaction is important for understanding the polymerization mechanisms. This is because the bulk polymerization of multifunctional systems is a complex process involving a plethora of reaction behaviors. The various phenomena of autoacceleration, unequal reactivity of different functional groups, multiple termination processes, volume shrinkage, and heterogeneities of the networks formed make understanding the mechanisms difficult. Thermal curing of the monomers (BHAPM and BHAPE) was carried out by scanning from room temperature to 300°C with the DSC-7 (PerkinElmer) at different heating rates of 5, 10, 15, and 20°C/min under an N$_2$ atmosphere. Each monomer was thoroughly mixed with 1 wt % benzoyl peroxide as the thermal initiator at room temperature. The mixture (10 mg) was placed in the DSC sample pan, and the instrument was scanned from 30 to 300°C at a constant heating rate. Typical DSC thermograms are shown in Figure 4 with large single exothermic peaks around 100°C. The maximum exothermic temperature (T_p) shifted toward a higher temperature
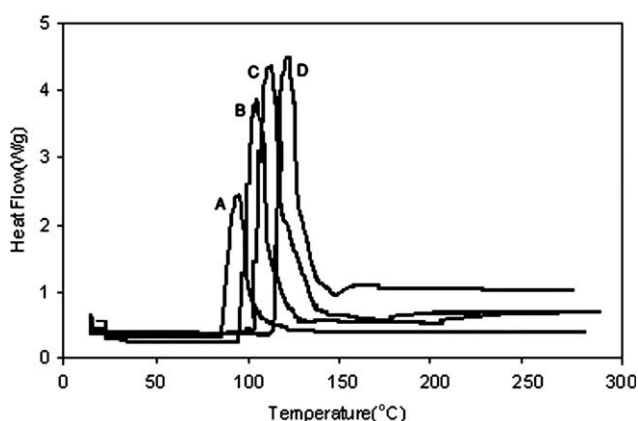
Figure 4 DSC thermograms of BHAPE cured with 1 wt % benzoyl peroxide at heating rates of (A) 5, (B) 10, (C) 15, and (D) 20°C/min.

TABLE I
DSC Data for the Curing Reaction of BHAPE

β (°C/min)	T_p (K)	$1/T_p$ × 10^3 (K^{-1})	Ln β	$-\ln(\beta/T_p^2)$	Exothermic heat (J/g)
5	366	2.70	1.61	10.19	66.25
10	380	2.63	2.30	9.58	64.58
15	385	2.59	2.71	9.20	48.53
20	393	2.54	2.99	8.95	37.01

with increasing heating rate from 5 to 20°C/min; this indicated that the maximum reaction rate occurred at higher temperatures when the time of heating decreased.

According to the method of Kissinger,[25] the activation energy (E_a) is obtained from the maximum reaction rate, where $d(d\alpha/dt)/dT$ is zero under a constant heating rate condition (where α is the degree of conversion and is generally defined as the total heat generated at time t with respect to the total heat of the reaction, and T is the temperature of the exothermic peak). The resulting relation for the analysis of the DSC data is expressed as follows:

$$-\ln(\beta/T_p^2) = E_a/RT_p - \ln(AR/E_a) \quad (1)$$

where T_p is the temperature at which the instant conversion rate is maximum, β is the constant heating rate, A is the frequency factor, and R is the gas constant. The E_a values were calculated from the slopes of the linear plots of $-\ln(\beta/T_p^2)$ against $1/T_p$.

The Ozawa–Flynn–Wall method[26] is an alternative method for the calculation of the E_a value and is expressed as follows:

$$\ln \beta_i = \text{Constant} - 1.052E_a/RT_p \quad (2)$$

The plot of $\ln \beta_i$, different heating rates, versus $1/T_p$ gives straight line with a slope of $1.052E_a/R$. Tables I and II give all the data obtained from the DSC experiments and used in the calculation of the E_a values according to eqs. (1) and (2). The calculated E_a values are given in Table III.

Absorption properties

Dimensional changes of resin composites during and after setting are a source of concern for applicants.

TABLE II
DSC Data for the Curing Reaction of BHAPM

β (°C/min)	T_p (K)	$1/T_p$ × 10^3 (K^{-1})	Ln β	$-\ln(\beta/T_p^2)$	Exothermic heat (J/g)
5	381	2.62	1.61	10.28	100.21
10	383	2.61	2.30	9.60	97.03
15	388	2.57	2.71	9.21	75.92
20	392	2.54	2.99	8.95	69.25

TABLE III
Values of the Kinetic Parameters

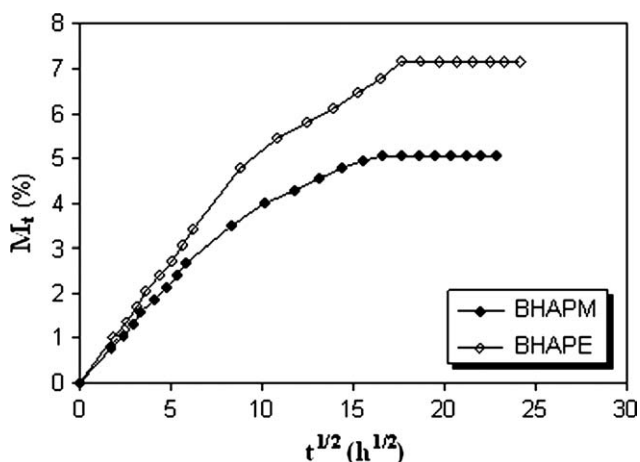| Monomer | E_a (kJ/mol) | | A (min^{-1}) | k (min^{-1})^a |
	Kissinger's equation	Ozawa's equation		
BHAPE	78.23	80.45	3.42×10^{10}	0.832
BHAPM	88.54	90.22	8.49×10^{11}	0.825

^{a} Arrhenius rate constant at 385°K.

The dimensional stability of resin composites is affected by polymerization shrinkage, thermal contraction and expansion, and interaction with an aqueous environment. The crosslinked network structure of a resin is expected to have water uptake, which is strongly bonded to the polar nature of the specific functional groups. The absorbed moisture can cause permanent chemical and physical changes by including crazes or microcavities and can, therefore, accelerate the moisture diffusion further.

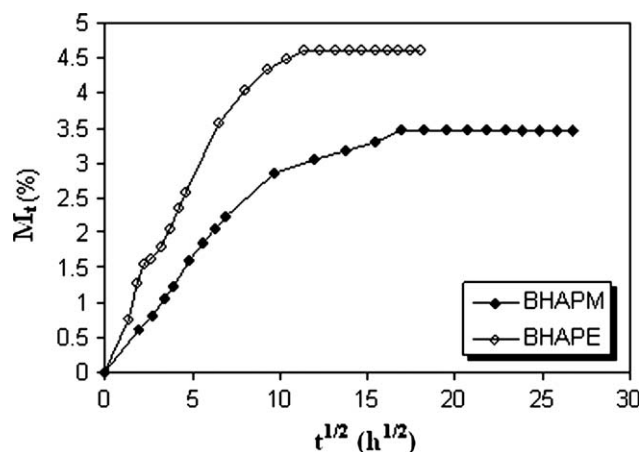The diffusion coefficient (D) is a function of the concentration of diffusant and is given by Fick's second law:

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \tag{3}$$

where $\partial C / \partial t$ is the diffusion rate and depends on the change in concentration (C) with the distance (x), $-\partial C/\partial x^2$.

The total amount of substance diffusing in the polymeric material (M_t) as a function of time is given by the integral of the solution of eq. (3) across the thickness (h) of the sample, and under specific conditions, such as when $D/h^2 \leq 0.05$, is expressed as follows:

Figure 6 Absorption behavior of the cured samples in basic solution.

$$\frac{M_t}{M_{max}} = \frac{4}{h\sqrt{\pi}} \sqrt{Dt} \tag{4}$$

where M_{max} is the maximum quantity of the diffusing substance at infinite time. The M_t (%) values were obtained from the water uptake of the three samples after exposure to identical conditions. The relative weight increase in each sample was calculated as follows:

$$\Delta m_{ti} = (m_{ti} - m_{0i})/m_{0i} \times 100 \tag{5}$$

The average weight increase was calculated as follows:

$$M_t(\%) = \sum_1^3 \Delta m_{ti}/3 \tag{6}$$

where m_{0i} is the initial weight of the sample before it is exposed to liquid, m_{ti} is the weight of the

Figure 5 Absorption behavior of the cured samples in distilled water.
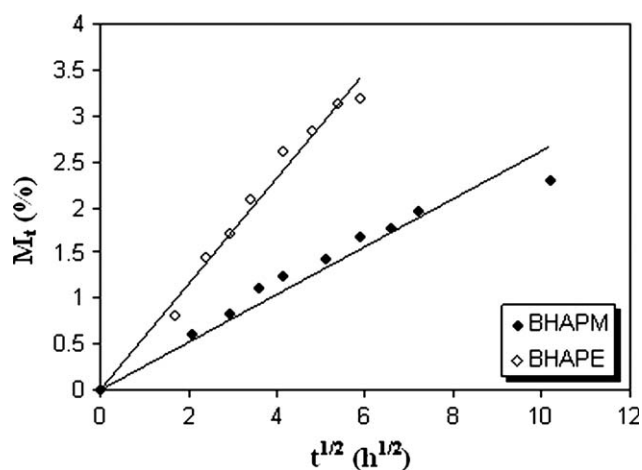
Figure 7 Linear regions of the acid absorption curves.

Monomer	D ($\times 10^{-12}$ m^2/s)		
	Water	NaOH 50%	H$_2$SO$_4$ 30%
BHAPM	3.30	3.52	3.78
BHAPE	4.38	4.84	5.57

sample after each period of exposure, and Δm_{ti} is the sum of three readings. D can be calculated from the slope of the linear region of the diffusion curve that is obtained by the fitting of the experimental values of water uptake M_t (%) versus $t^{1/2}$. The fitting of the experimental data resulted in the curves shown in Figures 5 and 6 for the samples exposed to distilled water and a base solution, respectively. From the linear fits in the first step of the M_t (%) versus $t^{1/2}$ ($h^{1/2}$) curves, shown in Figure 7 for the sample exposed to acid solution, the D values were calculated by means of the following expression. Three samples were used for the measurement of water absorption, and the reported value was the average of three readings:

$$m = \frac{\sqrt{D}4M_{\max}}{h\sqrt{\pi}} \tag{7}$$

where m is the slope of the fitting. The calculated D values are summarized in Table IV. In general, the behavior is similar to that predicted by Fick's law: (1) the sorption curves are linear in the initial stages, and (2) above the linear portions, the sorption curves are concave to the abscissa axis. As expected, a crosslinked network with the ether linkage in the polymer chain of BHAPE showed a higher water absorption in comparison with BHAPM. The equilibrium amounts of water absorption for BHAPE and BHAPM were 7 and 5%, respectively. As shown in Table IV, the cured samples had the highest value of D in the 30% acid solution and the lowest value of D in distilled water.

CONCLUSIONS

New methacrylate-based, curable macromonomers, BHAPE and BHAPM, were prepared by the reaction of GMA with DDE and DDM in the absence of solvent. The progress of the reaction was monitored by TLC and was followed by measurement of the disappearance of the absorption peak at 915 cm^{-1}, characteristic of terminal epoxy groups. FTIR and H-

NMR spectroscopy techniques were used to characterize the structure of the monomers. The thermal curing of the monomers mixed with benzoyl peroxide as the thermal initiator was carried out in a DSC at different heating rates under an N$_2$ atmosphere. The monomers were cured with the highest rate at 100°C, and the E_a values were in the range of 80–90 kJ/mol. The cured samples were tested for water absorption and stability in acid and base solutions at room temperature. The cured samples of BHAPE showed higher values of water absorption.

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