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Synthesis and molecular characterization of acrylate liquid crystalline resin monomers (ALCRM)

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Abstract

A novel biocompatible resin monomer 4-3-(acryloyloxy)-2-hydroxypropoxy) phenyl 4-(3-(acryloyloxy)-2-hydroxypropoxy) benzoate, as an oral restorative - acrylate liquid crystalline resin monomer (ALCRM) was synthesized. The intermediate product and the final product were characterized by differential scanning calorimetry (DSC), polarized optical microscope (POM), and nuclear magnetic resonance (NMR). A resin matrix which has a potential application in dental composites was prepared by photopolymerizing ALCRM and triethylene glycol dimethacrylate (TEGDMA) as a primary and diluted monomer with a photosensitizer of camphorquinone (CQ) and 2-(Dimethylamino)ethyl methacrylate (DMAEMA) mixture. The molar ratio of ALCRM and TEGDMA was 7:3. The properties such as the curing depth, curing time, and the volumetric shrinkage of the resin matrix were investigated and compared with a traditional composite resin matrix Bis-GMA. After photocuring polymerization, the conversion degree of the resin matrix is 68.06%, higher than Bis-GMA/TEGDMA; the curing time is 4.08±0.20min, the curing depth is 2.10±0.17mm, and the volumetric shrinkage is 3.62%±0.26%. All the properties exhibit a better performance of the prepared resin matrix than Bis-GMA.

Key words: Biocompatible resin, acrylic acid, degree of conversion, polymerizable shrinkage, photocuring.

Introduction

Biocompatible resin is a common material for restoration of tooth defect, which is mainly composed of resin matrix and inorganic fillers (1, 2). A notable disadvantage of commercial biocompatible resin is polymerizable shrinkage, so far the fillers have been developed to improve properties of material (3). Currently, modified resin matrix has attracted more attention, scientists hope to develop a resin matrix with "zero" polymerizable shrinkage (4). Due to the unique optical and mechanical properties, liquid crystal polymers have been widely investigated (5). In 2006, University of Texas Health Science Center developed a new bifunctional liquid crystal monomer that can be applied for oral restorative (5, 6). Recently, various liquid crystal resins have been developed by many research groups, the most significant advantage of the novel liquid crystal resin is extremely low polymerizable shrinkage (7-9). In this study, an acrylate liquid crystalline resin monomer (ALCRM) - 4-3-(acryloyloxy)-2-hydroxypropoxy) phenyl 4-(3-(acryloyloxy)-2-hydroxypropoxy) benzoate was synthesized and characterized, diluted monomer with a photosensitizer of camphorquinone (CQ) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) mixture was added to prepare a photocuring liquid crystal resin matrix that can be clinically used for oral restorative. The polymerizable shrinkage, degree of conversion, curing time and curing depth were determined and compared with traditional composite resin matrix Bis-GMA.

Materials and methods

Materials

The detailed synthesis of the 4-3-(acryloyloxy)-2-hydroxypropoxy) phenyl 4-(3-(acryloyloxy)-2-hydroxypropoxy) benzoate (ALCRM monomer) sample has been described in a recent publication (8). Bis-GMA and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%) were purchased from Sigma–Aldrich, St Louis, MO, triethylene glycol dimethacrylate (TEGDMA) was purchased from Wako and Guang Chun Le Co Japan, camphorquinone (CQ, 99%) was purchased from Alfa Aesar Co, Ward Hill, MA. All chemicals were used as received.

ALCRM monomer was mixed homogeneously with diluted monomer TEGDMA according to a ratio of 7:3 by weight and the mixture was kept in a sealed vial. The Bis-GMA in the control group was tested by the same method.

Determination of degree of conversion

Absorption spectrum of the monomer before photocuring was obtained by FTIR followed by addition of photoinitiator - lwt% CQ/2wt% DMAEMA. The light source is LED light with emission of visible light having wavelength above 400 nm. The distance between the sample and light source was 5 mm and irradiation time was 60 s. KBr plate was loaded with the same direction before photocuring the momoner, asorption spectrum of photocured sample was obtained. Degree of conversion (DC) was calculated according to the FTIR spectra before and after photocuring using eq 1 (10).

$$DC = \frac{\left(\frac{A_{1634}}{A_{1606}}\right)_0 - \left(\frac{A_{1634}}{A_{1606}}\right)_t}{\left(\frac{A_{1634}}{A_{1606}}\right)_0} \times 100\% \quad (1)$$

where DC is degree of conversion, A_{1634} is absorption peak area of double bond onto linear chain at the wavelength of 1634 cm^{-1}, A_{1606} is absorption peak area of double bond onto benzene ring at the wavelength of 1606 cm^{-1}, substript 0 and t repreant before and after photocuring, respectively.

The Bis-GMA in the control group was tested by the same method, the wavelenghes of absorption peaks of double bonds onto linear chain and benzene ring are at 1635 cm^{-1} and 1609 cm^{-1}, respectively.

Determination of curing time and depth

For curing time determination (11): the mononer with photoinitiator was loaded into a plastic cylinder with a diameter of 5 mm and a height of 3 mm, irradiated by curing light. From beginning of irradiation, upper and lower surfaces of the cylinder were detected by probes at an interval of 30 s until no indentation was detected. The requied time for photocuring monomer is the average of curing time of upper and lower surfaces. Each sample was determined 5 times, the result was calculated from the average of data ($\bar{X}$) and the standard deviation (S) was also calculated.

For curing depth determination: a plaster mold (8 mm height and 4 mm internal diameter) was put on a polyethylene film with a carrier film underneath. Bulk material before photocuring was filled into the mold and another polyethylene film covered the top, then the top carrier film was removed. The sample was irradiated for 40 s, and the sample was taken out of mold after 180±20 s, uncured materials were removed and height of cured sample was measured with a vernier caliper. Each sample was determined 5 times, the result was calculated from the average of data ($\bar{X}$) and the standard deviation (S) was also calculated.

The Bis-GMA in the control group was tested by the same method.

Determination of volumetric shrinkage

Volumetric shrinkage of the material was determined using a dilatometer assembled in this laboratory (8). The dilatometer is shown in Figure 1, which is composed of a scaled capillary and a tube loaded by sample and inflating medium. During the experiment, 5 mL sample was added into the tube and distilled water was also filled as medium. The tube and capillary were closly attached and vertically fixed by a clamp. 0.5 mL monomer misture was added into the diatometer, the sample was irradiated by LED curing light, the distance between the sample and light source is 1 mm. The sample was irradiated 9 times from various directions (see the direction of arrows in Figure 1) and each irradiation time was 40 s. Volumetric shinkage of sample was calculated according to eq 2 by the change of the scale of capillary before and after photocuring. Each sample was determined 5 times at room temperature, the result was calculated from the average of data ($\bar{X}$) and the standard deviation (S) was also calculated.

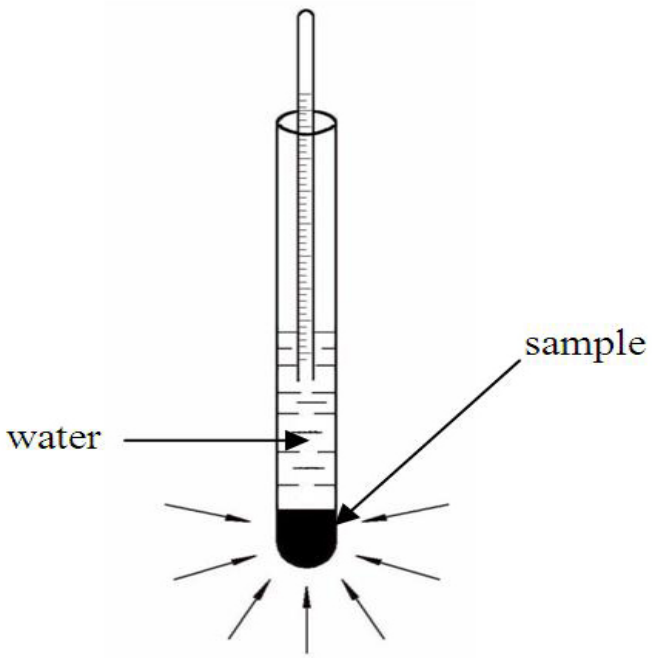

Figure 1. schematic diagram of liquid dilatometer.

$$VH = \frac{\Delta V}{V_0} \times 100\% \quad (2)$$

where VH is rate of volumetric shinkage of sample, V_0 is the sample volume before photocuring and ΔV is volumetric change of capillary.

The Bis-GMA in the control group was tested by the same method.

Results

Characterization of ALCRM

The detailed synthesis of the ALCRM monomer sample has been described in a recent publication (8). The ^{1}H NMR spectrum for purified ALCRM monomer is shown in Figure 2. ^{1}H NMR ($CDCl_3$): δ 7.45 (4H), δ 6.95-6.93 (4H), δ 6.42-6.38 (1H), δ 6.16-6.09 (1H), δ 5.83-5.80 (1H), δ 4.18 (2H), δ 3.99 (4H), δ 1.85-1.69 (6H).

The DSC curve of ALCRM monomer is shown in Figure 3. Five endothermal peaks are observed from Figure 3, the first peak appears at -70°C, which might be due to instability of the instrument. The second peak is from -30°C to 0°C with a basically constant enthalpy value, indicating that the monomer starts to melt and representing the glass transition temperature (T_g) of ALCRM monomer. The third peak appears at 18°C, representing the melting temperature (T_m) of ALCRM monomer. An obvious endothermal peak exhibits at around 30°C, which is the temperature that the liquid crystal monomer transfers from highly ordered semectic to lower ordered nematic. The last peak appears at around 42°C, which represents the cleaning point of liquid crystal monomer. The monomer is transferred from anisotropic phase to isotropic phase at around this temperature and liquid crystal phase disappears.

During POM detection, it can be observed that field of view was always dark without any bright cluster spots when temperature decreased from 100°C to 45°C. At around 43°C, field of view displayed a mixture of continuous bright fields and bright orange cluster spots,

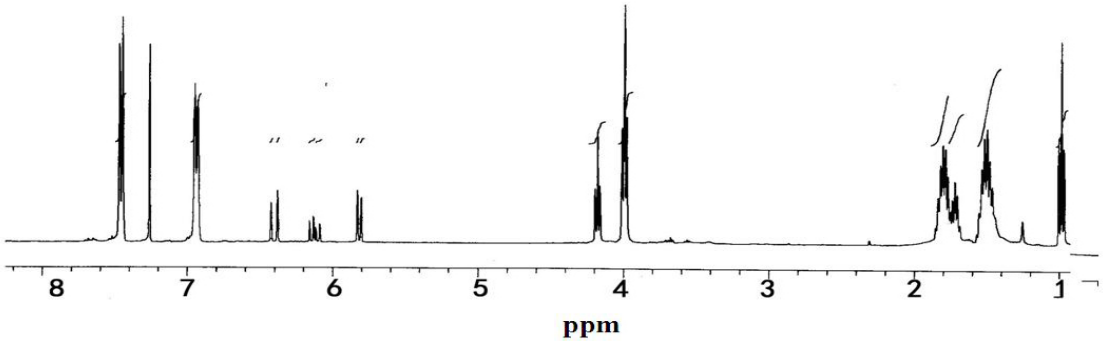

Figure 2. ^{1}H NMR spectrum of ALCRM monomer.

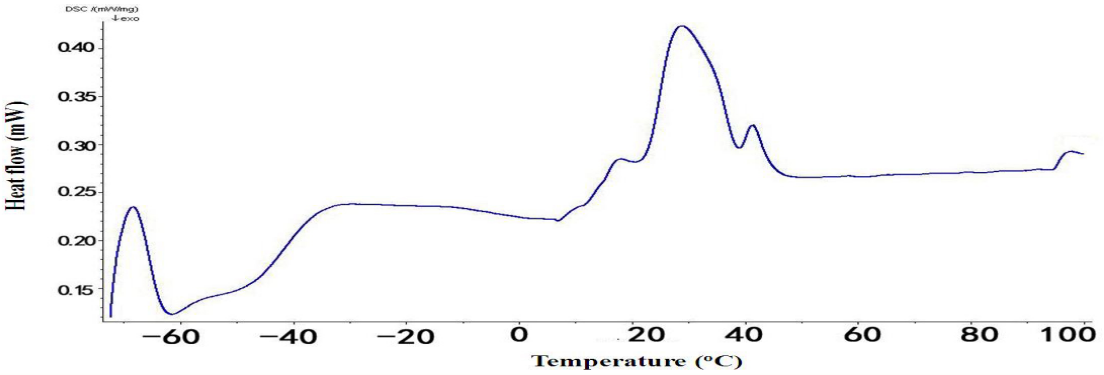

Figure 3. DSC curve of ALCRM monomer.

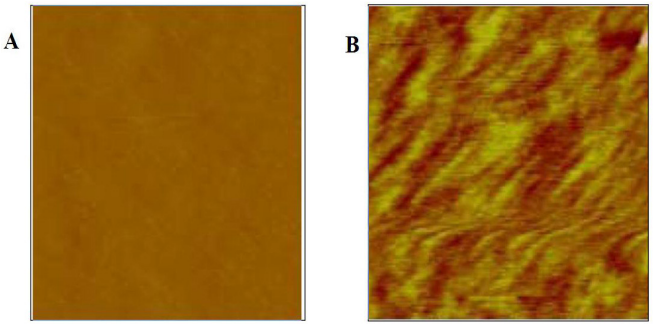

Figure 4. (A) POM picture of ALCRM monomer at 45°C and (B) POM picture of ALCRM monomer at 25°C.

the monomer is transferred from anisotropic phase to isotropic phase at this temperature. At around 18-28°C, bright orange cluster spots extended and formed a banded texture structure which was interwoven with orange and yellow, exhibiting a typical liquid crystal structure. With a decrease in temperature, the filed of view turned dark again at around -30°C, ALCRM monomer was transferred to crystalline state, no any bright cluster spots or bright bands could be observed. POM picture (×400) of ALCRM monomer taken at around 45°C is shown in Figure 4A. At this time temperature was above the cleaning point and ALCRM monomer exhibited isotropic. POM picture (×400) of ALCRM monomer taken at room temperature (around 25°C) is shown in Figure 4B, bright banded texture interwoven with orange and yellow could be observed, which characterizes texture structure of liquid crystal.

Determination of DC

FTIR spectra of ALCRM monomer and the control group before and after photocuring are shown in Figure 5. DC of the experimental and control groups were calculated based on the spectra in Figure 5 and Eq 1, the results are listed in Table 1.

Determination of curing time, curing depth and volumetric shrinkage

The results of curing time, curing depth and volumetric shinkage obtained with experimantal group and control group are listed in Table 2. Statistical analysis was conducted to the results in two resin matrix using

Table 1A. The peak area of the double bond and the phenyl group in the FTIR spectra values of ALCRM /TEGDMA and Bis-GMA/ TEGDMA.

Group	Before cure		After cure	
	linear double bond	phenyl double bond	linear double bond	phenyl double bond
ALCRM/TEGDMA	144.190	151.199	206.415	680.932
Bis-GMA/TEGDMA	540.751	198.792	294.855	196.605

Table 1B. DC values of ALCRM /TEGDMA and Bis-GMA/ TEGDMA.

Group	ALCRM/TEGDMA	Bis-GMA/TEGDMA
DC	68.06%	45.86%

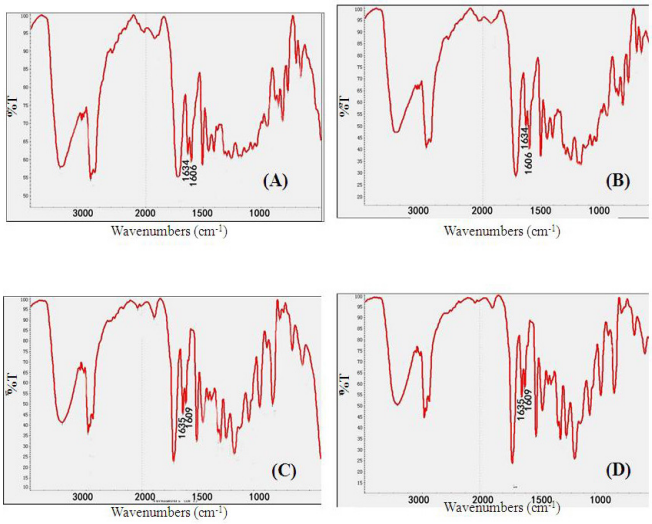

Figure 5. FTIR spectra of uncured (A) and photocured (B) ALCRM/TEGDMA and FTIR spectra of uncured (C) and photocured (D) Bis-GMA/TEGDMA.

Student-Newman-Keuls method. Volumetric shrinkage of experimental group is lower than that of control group, they have significant difference (p<0.05). Curing depth and curing time of experimental group are lower, and higher, respectively than that of control group, they both have significant difference (p<0.05).

Determination of vickers hardness (VHN)

HBRV-1857.5 hardness meter was used to measure YHN of the resin. The loading sample was 30 kgf, then picked up the sample and measured the length of the diagonal line with a microscope, found the hardness values from the reference table. The average value of a set of values ($\overline{X}$) was used as the experimental result with three digit numbers, the standard deviation (S) was calculated. Table 3 lists the compressive strength in MPa and the vickers hardness (VHN) of experimental dental resin composite.

Discussion

ALCRM, Bis-GMA and TEGDMA are acrylate resins (12). Usually the DC of monomer is calculated by the overlap of absorption peaks of phenyl double bonds, as an internal standard of this type of resin (10), the overlap of absorption peaks of linear double bonds does not have a significant effect on DC (the double bonds of CQ+DMAEMA are all located onto linear chain) (13). In this study, the double bonds of ALCRM phenyl ring show an absorption peak at 1606 cm^{-1}, however, the double bonds of Bis-GMA phenyl ring show an absorption peak at 1609 cm^{-1}, the difference in the position of peak is due to the shift of absorption peak affected by molecular medium crystal during test. Figure 5 shows that before and after photocuring, the relative ratios of absorption peaks of linear double bond at 1635 cm^{-1} and 1634 cm^{-1} to absorption peaks of phenyl double bond at 1609 cm^{-1} and 1606 cm^{-1} are both changed, suggesting that ALCRM and Bis-GMA respectively polymerized with TEGDMA.

DC of ALCRM monomer is higher than that of Bis-GMA due to acrylate end-capped liquid crystal monomer. The ester groups which are located at the end of acrylate and methacrylate are electrophilic, but the electron-donating capacity of methyl group on α-position of Bis-GMA is much stronger than that of hydrogen on α-position of ALCRM, the latter can not provide enough electrons to ester group, therefore the electron clouds distribution is inhomogeneous with stronger activity. Moreover, because the steric hindrance effect of methyl group is stronger than that of hydrogen, the chain end activity of acrylates is stronger than that of methacrylates, DC of acrylate monomers is higher (14). Currently some scientists have tried to add nano-fillers with different diameters (15) or different photoinitiating systems (16) in Bis-GMA matrix to improve DC of resin monomer and to increase strength of materials. However, there has been no studies on improvement of monomer DC using modified resin matrix (17).

Polymerization shinkage is closly related to long-term effect of oral restorative, the greatest advantage of liquid crystal resin is low curing shrinkage rate (15). The polymerization shinkage rate of ALCRM monomer is smaller than that of Bis-GMA, because liquid crystal resin matrix contains medium crystal which is composed of rigid rod-like molecules having a certain length-diameter (L/D) ratio. The molecular weights of these molecule are large and the ratio (L/D) is approximately (4~8):1. Before polymerization, the molecules arrange orderly in area of their mesomorphic phase, they parallel arrange along the direction of long axis and polymerization was initiated under light curing (18). Although the ordered arrangement of molucules was disorganized to form a network structure during polymerization, as long as the liquid crystal resin monomer is garanteed to polymerize within its mesomorphous range (the meso-

Table 2. Curing time, curing depths and polymerization shrinkage rate (%) of ALCRM /TEGDMA and Bis-GMA/TEGDMA photocuring.

	ALCRM/TEGDMA	Bis-GMA/TEGDMA
Curing time (min)	4.08 ± 0.20	3.63 ± 0.34
Curing depth (mm)	2.10 ± 0.17	3.06 ± 0.26
Rate of volumetric shringkage (%)	3.62 ± 0.26	5.80 ± 0.44

Table 3. The compressive strength and VHN of resin composite.

Resin molar ratio (ALCRM:TEGDMA)	compressive strength (Mpa)	VHN
7:3	197.6 ± 5.59	27.56 ± 0.42

morphous range of ALCRM synthesized in this study is 18-42°C, room temperature), the special properties of liquid crystal polymer can be reserved after photocuring (namely "memory effect") (7, 8). Furthermore, as long as a liquid crystal monomer is cured within its mesomorphous range, during polymerization the rod-like structure of monomer molucules will naturally bend to expand, which is able to counteract the shinkage result from replacement of Van der Waals bond by covalent bond due to loose molecules in polymerization. Lastly, the molecular weight of ALCRM is higher than that of Bis-GMA, when they have the same mass, ALCRM possesses less number of molecules, overall shrinkage of intermolecular distance is less comparing Bis-GMA in polymerization (19).

Curing time of oral resin composite is important to clinical operation, because polymerization is initiated in oral environment where the conditions of operation are relatively complicated, some restrictions like the size of the oral opening, moisture protection to saliva, etc require the reaction system to initiate polymerization as soon as possible. The requirements of an initiator for oral liquid crystal resins are different with industrial liquid crystal resins. Generally, industrial liquid crystal resins are prepared by thermal curing, but most oral resin composites are polymerized by photocuring. The liquid crystal resin in this study was synthesized via photocuring (20). Comparing the traditional thermal polymerized liquid crystal resin, the advantage of photopolymerization is that the curing temperature can be selected in the range of liquid crystal phase (the mesomorphic range of ALCRM is 18-42°C). Molecular orientation and polymerization are completely separated, and polymerization can be initiated after orientation. Thus, the highly ordered structure of liquid crystal monomer is reserved after curing. However, because ALCRM monomer polymerize after orientation via photocuring, the curing time of ALCRM is longer than the curing of Bis-GMA. The curing depth is a little deficient comparing Bis-GMA within the same time. This problem might be solved by clinical layer-by-layer curing technique in the future.

In this paper, a novel biocompatible resin monomer - acrylate liquid crystalline resin monomer (ALCRM) was synthesized. ALCRM can be used as a potential oral restorative clinically. The final product was characterized by DSC, POM, and ^{1}H NMR. ALCRM monomer can undergo copolymerization with a diluted monomer TEGDMA, which is commonly used in oral treatment. The properties of ALCRM/TEGDMA and Bis-GMA/TEGDMA photocuring systems were compared. It has been found that DC of ALCRM monomer was 68.06% via photopolymerization, higher than that of Bis-GMA. The photocuring time of ALCRM/TEGDMA was longer than that of Bis-GMA/TEGDMA, curing depth of ALCRM/TEGDMA was a little deficient. Under the same polymerization conditions, the polymerization shrinkage of ALCRM/TEGDMA was smaller than that of Bis-GMA/TEGDMA.

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