Synthesis and FTIR Spectroscopic Investigation of the UV Curing Kinetics of Telechelic Urethane Methacrylate Crosslinkers Based on the Renewable Resource—Cardanol

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ABSTRACT: UV curable telechelic urethane–methacrylate crosslinkers based on the natural resource—cardanol was synthesized in a one pot synthetic step involving end capping of isophorone diisocyanate with one equivalent of hydroxyethyl methacrylate followed by condensation with cardanol. The structures of the resins were characterized by ^{1}H and ^{13}C NMR, fourier transform infrared (FTIR) and Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectroscopies and size exclusion chromatography (SEC). The curing process and double bond conversion in presence of 2,2-diethoxy acetophenone as photoinitiator upon UV irradiation was followed by Fourier transform infrared spectroscopy. These hydrogen bonded crosslinkers based on cardanol and its derivatives had higher double bond conversion when compared to a non-hydrogen bonding standard such as hexanediol diacrylate (HDDA) under identical conditions. The temperature effects on the hydrogen bonding were investigated, and a decrease in the extent of double bond conversion with increase in temperature was observed for the telechelic urethane–methacrylate crosslinkers whereas a steady increase in the curing rate was observed for HDDA. This gives direct indication of the influence of hydrogen bonding on the curing process. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2781–2790, 2008

Key words: UV curing; hydrogen bonding; renewable resource; infrared spectroscopy; cardanol

INTRODUCTION

UV radiation curing is one of the efficient technologies which has found potential applications in wide variety of areas. Because of its high cure speed, solvent free characteristics, ambient temperature operations, and low energy consumptions this method has found applications in the coating industry, ink industry, and in microelectronics.[1–4] Moreover, UV-cured polymers are known to exhibit superior chemical and heat resistance as a result of their high crosslink density. In addition, their mechanical properties can be adjusted in a wide range by a proper choice of the telechelic oligomer, from soft and flexible composite materials to hard and tough organic glasses. The most commonly used resin chemistry in UV curing applications is the one based on acrylics among which the urethane acrylates are known for their best mechanical properties and chemical resistance. The advantages of a urethane unit in the radiation curable crosslinker is that it introduces hard segments into an otherwise soft block segment, thus giving rise to micro-phase separated domains.[5–8] Hydrogen bonds from the urethane groups of the hard segments give rise to a physical network which accounts for many of the desired properties like tensile strength, elongation, and improved surface wetting.[9] The influence of the hydrogen bonding is not only restricted to the properties of the resultant cured coatings but also has an effect on the cure speed.

In recent years the utilization of bio resources to obtain value-added products has attracted much attention because they are obtainable from natural resources. In this respect, cardanol a hazardous by-product obtained by the complete distillation of cashew nut shell liquid (CNSL) plays a significant role for preparing cost effective materials. Cardanol is the main component obtained by the double distillation of CNSL, which is a phenolic derivative having unsaturated 15-carbon side chain having 1–3 double bonds.[10–12] The long chain in the cardanol

imparts flexibility due to internal plasticizing. Because of its versatile nature, cardanol has various potential industrial applications such as resins, surface coatings, rubber compounding, friction lining materials, lamination, paints, and other miscellaneous applications.[12–14] The most obvious and common method of obtaining polymeric material from CNSL has been its polycondenzation with formaldehyde or formaldehyde containing materials.[15] However, the reactivity of the hydroxyl phenyl group of cardanol can be made use of to develop a variety of structurally diverse functional molecules.[16,17] Recently there are reports on the use of cardanol for preparing nanotubes, liquid crystalline polymers, polyurethanes etc.[18–21]

Speed of photocuring is an important factor as far as applications are concerned and in this respect resins that have an inherent ability to undergo faster curing are a cost effective investment. Decker et al. reported on new class of acrylates with a high intrinsic reactivity.[22] Jansen et al., Hoyle et al., and Bowman et al. reported on the influence of hydrogen bonding on the rate of photopolymerization.[23–25] Previously, we described the synthesis and properties of telechelic urethane methacrylates based on the cycloaliphatic unit—tricyclodecane dimethanol and poly(propylene glycol) (PPG) where we showed that hydrogen bonding brought about by the urethane unit in these systems induced a faster curing rate compared to analogous references that lacked the urethane unit.[26,27] Here, we report the facile synthesis of telechelic urethane–methacrylate UV curable crosslinkers based on functionalized cardanol and its saturated analogue-3-pentadecyl phenol. This is the first report of synthesis of urethane methacrylates based on cardanol.[28] It has been shown that renewable resources like castor oil and its derivatives can act as plasticizers when incorporated in coating resins.[29] Using these functional plasticizers, excellent elastic coatings exhibiting the slow release properties can be obtained without the plasticizers being able to migrate from the coating and thus causing subsequent embrittlement. It is expected that the new class of telechelic urethane–methacrylate UV curable crosslinkers developed based on cardanol and its derivatives would be able to impart mechanical stability and find applications in coating industry as well as other applications.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI), 2-hydroxyethyl methacrylate (HEMA), dibutyltindilaurate (DBTDL), 3-pentadecyl phenol, 2,2-diethoxy acetophenone,

were purchased from Aldrich and used as received. 3-chloro-1,2-propanediol was purchased from Aldrich and distilled before use. N,N-dimethylformamide (DMF) was purified by keeping it overnight over KOH followed by decanting and vacuum distilling. Cardanol was purchased from Vijayalekshmi Cashew Industry, Kollam, India.

Measurements

NMR spectra were recorded using 300-MHz Brucker NMR spectrophotometer in $CDCl_3$ containing small amounts of TMS as internal standard. The purity of the compounds was determined by JEOL JSM600 fast atom bombardment (FAB) high-resolution mass spectrometry as well as MALDI-TOF analysis. The matrix used was 2,5 dihydroxy benzoic acid dissolved in $CHCl_3$ which was spotted on MALDI target and allowed to dry before introducing into the mass spectrometer. Infrared spectra were recorded using a Perkin–Elmer, Spectrum one FTIR spectrophotometer providing unpolarized light at a scan rate 5 scans/min with resolution 4.00 cm^{-1}. The liquid samples or dilute solution of the solid samples in dichloromethane were spread over Potassium Bromide (KBr) plates and their spectra were recorded. IR spectra were recorded in the range of 4000–400 cm^{-1}. The molecular weights of the oligomers were also determined by gel permeation chromatography (GPC) in THF with polystyrene standards for the calibration. Waters 515 Pump connected through three series of Styragel HR columns (HR-3, HR-4E, and HR-5E) and Waters Model 2487 Dual Wavelength UV-Vis Detector and a Waters 2414 Differential Refractometer was used for analyzing the samples. The thermal stability of the crosslinked polymers was determined using DTG-60 Shimadzu thermogravimetric analyzer at a heating rate of 10°C/min in nitrogen and the instrument was calibrated with α- Alumina(α-Al_2O_3) standard. DSC measurements were performed on a DSC-Perkin-Elmer Pyris 6 DSC instrument at a heating rate of 10°C/min under a 20 mL/min purge of dry nitrogen atmosphere. Typically, 2–3 mg of samples was placed in an aluminum pan, sealed properly, and scanned from 10 to 280°C. The instrument was calibrated with indium, tin, and lead standards before measurements. All samples were first heated to melting and held for 3 min before their thermograms were recorded to remove their previous thermal history. WXRDs of finely powdered crosslinked polymer films were recorded by a Philips analytical diffractometer using CuKα emission. The spectra were recorded in the range of 2θ = 0–50 and analyzed using X'Pert software.

UV-curing studies

Thin films of the samples were prepared using laboratory draw down device to obtain $\sim$ 150 μm thick films. The samples dissolved in minimum quantity dichloromethane were mixed with 5 wt % of the photoinitiator 2,2-diethoxy acetophenone and drawn on KBr plates. The initial FTIR spectra was recorded as the t = 0 reading, and then the KBr plate along with its holder were subjected to the UV irradiation by using Dymax light curing device (Blue Wave 50AS model 39370) with a distance of 1 cm from lamp (Intensity of 18 mW/cm^2) to specimen at ambient temperatures in the presence of air. At definite time intervals their FTIR spectra were recorded to follow the disappearance of the double bond peak for kinetic analysis. Typically the methacrylate double bond conversion was followed by monitoring the disappearance of the peak at 815 cm^{-1}. The spectra recorded in the absorbance mode were normalized with the carbonyl peak $\sim$ 1728/1717 cm^{-1} as the internal standard. For the variable temperature UV curing studies also films of $\sim$ 150 μm thickness were drawn on KBr plates which were kept on a hot plate maintained at each particular temperature. The heater was placed inside the homemade UV curing chamber at a distance of 1 cm from the lamp and FTIR spectra were recorded at regular intervals of time to follow the disappearance of the methacrylic double bond at 815 cm^{-1}.

Synthesis of modified cardanol propane diol: 3-[(E)-3-pentadec-8-enyl)-phenoxy]-propane-1,2-diol

About 10 g (0.033 mol) of distilled cardanol was added to a mixture of 7.32 g (0.066 mol) of 3-chloropropane-1,2-diol and 2.65 g (0.066 mol) NaOH 2.65 g (0.066 mol) taken in 30 mL of 1 : 1 ethanol-water mixture in a round bottom flask. This mixture was refluxed for 36 h and then cooled to room temperature. For workup, the contents of the flask were poured into 300 mL water and extracted with dichloromethane (DCM). The organic layer was dried over anhydrous sodium sulfate and evaporated to get the product as a viscous liquid. Yield = 10.88 g (87%). ^{1}H NMR (300 MHz, CDCl$_3$, δ ppm): 7.17 (t, 1H, Ar—**H**); 6.80–6.70 (m, 3H, Ar—**H**); 5.37–5.32 (m, 2H, **CH**=**CH**, side chain unsaturation of cardanol); 4.09–4.01 (3H, Ar—O**CH₂CHO**HCH₂OH); 3.81–3.74 (m, 2H, OCH₂CHO**HCH₂OH**); 2.58 (t, 2H, Ar—**CH₂**) ; 2.04 (m, 4H, —**CH₂**CH=CH**CH₂**— of side chain unsaturation); 1.61 (m, 2H, Ar—CH₂ **CH₂**—); 1.37–1.25 (m, 16H, aliphatic protons of side chain); 0.91 (t, 3H, —**CH₃** of side chain). ^{13}C NMR (75MHz, CDCl$_3$, δ ppm): 157.9, 145.3, 130.6, 129.7, 122.5, 112.9, 111.7, 71.1, 68.6, 63.8, 36.2, 32.1, 31.6, 29.9, 29.8, 29.6, 29.5, 22.8, 14.2. FTIR (cm^{-1}): 3430,

3010, 2921, 1682, 1599, 1488, 1448, 1260, 1202, 1047, 933, 874, 775, 694. FAB-HRMS (MW: 376.58): Mass obtained (m + Na = 399.21).

A similar procedure was adopted for the modification of 3-pentadecyl phenol. 2.5 g (0.0083 mol) of 3-pentadecylphenol, 2.27 g (0.02 mol) of 3-chloropropane-1,2-diol and 1.0 g (0.025 mol) NaOH were refluxed for 36 h in 20 mL of 1 : 1 ethanol-water mixture in a round bottom flask. The product 3-(3-Pentadecyl-phenoxy)-propane-1,2-diol was then purified by column chromatography on a 100–200 mesh silica gel column using hexane/ethyl acetate (80 : 20 v/v) solvent mixture.

Yield = 2.47 g (77%). ^{1}H NMR (300 MHz, CDCl$_3$, δ ppm): 7.21 (t, 1H, Ar—**H**); 6.82–6.66 (m, 3H, Ar—**H**); 4.11–4.01 (3H, Ar—O**CH₂CHO**HCH₂OH); 3.87–3.72 (m, 2H, OCH₂CHO**HCH₂OH**); 2.79 (t, 2H, Ar—**CH₂**); 1.61 (m, 2H, Ar—**CH₂CH₂**—); 1.37–1.25 (m, 16H, aliphatic protons of side chain) 0.91(t, 3H, —**CH₃** of side chain). ^{13}C NMR (75 MHz, CDCl$_3$, δ ppm): 157.9, 145.3, 130.6, 129.7, 122.5, 112.9, 111.7, 36.3, 31.6, 31.3, 29.7, 29.3, 22.8, 14.1. FTIR (KBr, cm^{-1}): 3339, 2917, 2850, 1614, 1583, 1471, 1298, 1158, 1113, 1066, 1039, 931, 864, 771, 757, 717, 689, 619. FAB-HRMS (MW: 378.60): Mass obtained (m + Na = 400.85).

Synthesis of telechelic urethane–methacrylate of modified cardanol propanediol: (HEMA-IPDI)₂MCP or (MCPIH)

About 1.95 g (0.0088 mol) of isophorone diisocyanate (IPDI) in 10 mL dry DMF was taken in a 100 mL two-necked RB flask and the contents were cooled with ice. 1.14 g (0.0088 mol) of hydroxyethyl methacrylate (HEMA) was added dropwise with constant stirring under nitrogen over a period of 0.5 h. It was then brought to room temperature and left stirring for an additional 2 h. Three drops of dibutyl tin dilaurate (DBTDL) were added as catalyst, followed by dropwise addition of cardanol (1.5 g, 0.0039 mol) in 5 mL dry DMF under ice cold conditions. The reaction mixture was stirred for an additional 0.5 h at room temperature and then slowly heated to 55°C for 6 h. The contents were poured into 300 mL water and extracted with dichloromethane. The extract was washed with plenty of water and 5% NaOH solution, dried over anhydrous sodium sulfate, concentrated, and dried in vacuum oven at 60°C for 2 h. Yield: 66% (2.63 g).

^{1}H NMR (300 MHz, CDCl$_3$, δ ppm): 7.22 (t, 1H, Ar—**H**); 6.77–6.74 (m, 3H, Ar—**H**); 6.14, 5.59 (2s, 4H, —**CH₂**=C of HEMA); 5.39–5.34 (m, 2H, **CH**=**CH**, side chain unsaturation of cardanol); 4.31–3.99 (13H, Ar—O**CH₂CHCH₂**, 2—O**CH₂**—**CH₂**—O); 2.96 (4H, side chain of IPDI); 2.59 (t, 2H, Ar—**CH₂**); 2.02 (m, 4H, —**CH₂**CH=CH**CH₂**— of side chain unsatura-
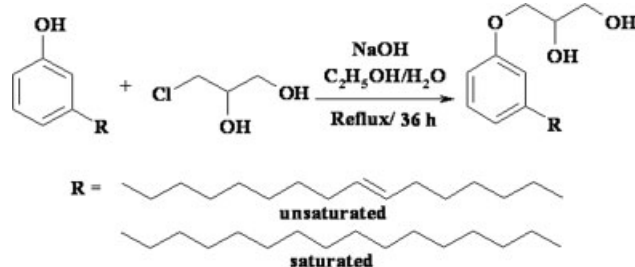
Scheme 1 Synthesis of modified cardanol.

tion); 1.98 (s, 6H, **CH$_3$** of HEMA); 1.70 (m, 2H, Ar—**CH$_2$CH$_2$**—); 1.31–1.25 (m, 46H, aliphatic protons); 0.93 (t, 3H, —**CH$_3$** of side chain). ^{13}C NMR (75 MHz, CDCl$_3$, δ ppm): 167.4, 158.4, 144.6,136.1, 130.3, 130.1, 129.9, 126.1, 121.3, 114.8, 111.4, 68.9, 66.9, 62.8, 46.2, 36.3, 31.3, 29.6, 29.3, 29.2, 29.1, 28.8, 27.6, 23.1, 22.5, 18.2, 14.1. FTIR (KBr, cm^{-1}): 3365, 2923, 2852, 1717, 1635, 1559, 1454, 1385, 1239, 1152, 1045, 949, 866, 812, 773, 695. MALDI-TOF (MW: 1081.45): Mass obtained (M—CH$_3$)$^+$ = 1066.6).

Saturated cardanol (3-pentadecyl phenol) based telechelic urethane–methacrylate (HEMA-IPDI)$_2$ MSCP or (**MSCPIH**) was synthesized adopting a similar procedure using 1.4 g (0.0063 mol) isophorone diisocyanate (IPDI), 0.825 g (0.0063 mol) HEMA and 1 g (0.0026 mol) of propane-diol modified 3-penta decyl phenol. Yield: 67% (2.18 g). ^{1}H NMR (300 MHz, CDCl$_3$, δ ppm): 7.16 (t, 1H, Ar—**H**); 6.91-6.73 (m, 3H, Ar—**H**); 6.14, 5.93 (2s, 4H, —**CH$_2$**=C of HEMA); 4.63–3.77 (13H, Ar—**OCH$_2$CHCH$_2$**, **2—OCH$_2$—CH$_2$**—O); 2.93 (4H, side chain of IPDI); 2.55 (t, 2H, Ar—**CH$_2$**); 2.17 (s, 6H, **CH$_3$** of HEMA); 1.69 (m, 2H, Ar—**CH$_2$CH$_2$**—); 1.25–1.05 (m, 54H, aliphatic protons); 0.97 (t, 3H, —**CH$_3$** of side chain). ^{13}C NMR (75 MHz, CDCl$_3$, δ ppm): 167.2, 158.3, 144.1,137.2, 129.9, 126.1, 121.5, 114.4, 111.1, 68.9,66.5, 62.8, 46.2, 36.3, 31.9, 31.3, 29.7, 29.4, 28.8, 27.6, 23.1, 22.5, 18.2, 14.3. FTIR (KBr, cm^{-1}): 3355, 2925, 2853, 1709, 1640, 1560, 1463, 1386, 1365, 1307, 1242, 1155, 1047, 952, 869, 812, 774, 718, 695.

RESULTS AND DISCUSSION

Synthesis and structural characterization

Commercially obtained cardanol is a mixture of four components differing in the degree of unsaturation of the C$_{15}$-alkyl side chain ranging from fully saturated to triene.[12] Commercial cardanol was purified by double vacuum distillation and characterized by means of ^{1}H NMR, FAB Mass, and FTIR spectroscopic analysis. The mass spectra of the final distilled product showed a single sharp peak at 302 m/z confirming that the cardanol sample had only one double bond in the C$_{15}$ side chain. Modifi-
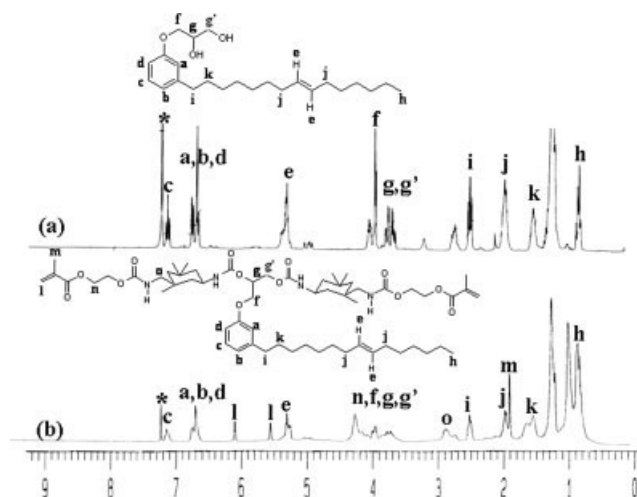
Figure 1 ^{1}H NMR spectra of modified cardanol - MCP (a) and cardanol urethane–methacrylate monomer -MCPIH (b).

cation of cardanol was achieved by coupling the phenolic OH group with 3-chloropropane-1,2-diol in presence of sodium hydroxide as base in ethanol water mixture as shown in Scheme 1. Figure 1(a) shows the proton NMR spectra of cardanol modified with propanediol (MCP). New peaks corresponding to the alkyl protons of the propane diol unit appear in the region ∼ 4 ppm. The corresponding analogue based on 3-pentadecyl phenol (MSCP) was purified using column chromatography to remove unreacted starting material. The single sharp peak in the size exclusion chromatogram (SEC) shown in Figure 2 along with the molecular ion peak in the FAB mass spectra confirmed the purity of both the modified products. The telechelic urethane–methacrylate crosslinkers were synthesized by first end capping isophorone diisocyanate with hydroxyethyl methac-
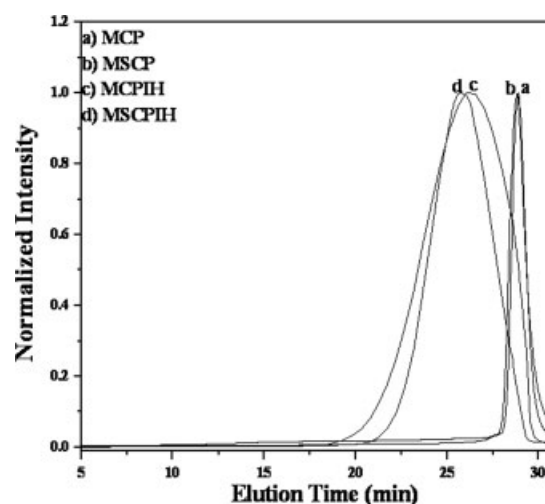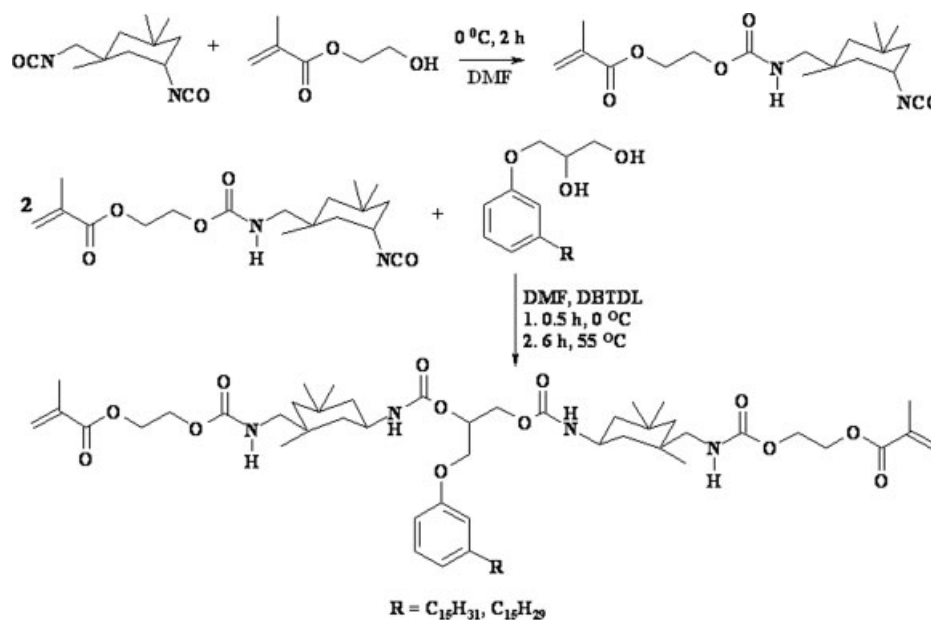

Figure 2 GPC chromatograms of modified cardanol, modified 3-pentadecyl phenol and the corresponding crosslinkers.

Scheme 2 Synthesis of telechelic urethane methacrylates MCPIH and MSCPIH.

rylate followed by condensation with MCP or MSCP. The reaction scheme and the structure of the crosslinkers are given in Scheme 2. The proton NMR spectra of the final product showed a slightly more than expected value for integration of the aromatic protons indicating presence of small amounts of unreacted MCP/MSCP. This was reflected in their SEC (Fig. 2) also which showed a slightly broad distribution of molecular weight. The synthesis was also attempted by first coupling MCP or MSCP with isophorone diisocyanate to generate oligomers followed by end capping with HEMA. However, in this procedure the extent of incorporation of HEMA was very minimal as indicated by the integration of the proton peaks of double bond from HEMA part in the ^{1}H NMR spectra. Therefore, the first procedure was adopted for the synthesis of the telechelic urethane methacrylates. In the case of reactions involving IPDI, there are two possible sites for reaction—one at the primary isocyanate and the other at the secondary isocyanate. Ideally this can be controlled through the control of the reaction conditions, for instance, in our reaction the first step i.e., reaction of HEMA with IPDI was carried out at room temperature, followed by the second step i.e., reaction with MCP or MSCP under more vigorous conditions in presence of added catalyst and higher temperatures. This second step also involves the reaction of both primary and secondary type of hydroxyl groups with the isocyanate. The vigorous conditions and longer reaction times ensure the reaction of both types of hydroxyl groups. The samples were subjected to MALDI-TOF analysis using 2,5-dihyroxy benzoic acid as the matrix and the spectra for

MCPIH is given in Figure 3. Molecular ion peaks were obtained for either $[M-CH_3]^+$ or cationic species such as (M-2HEMA)Na+ or [M-2HEMAC(O)O]2Na+ where the sodium ions are from the solvents. The presence of fragments corresponding to biscoupled product along with a complete absence of peaks corresponding to monocoupled product confirmed the formation of the desired biscoupled product. The monocoupled product has an expected mass of 728 U; however, no peaks were observed with mass lower than 800 U.

UV-radiation curing

The telechelic urethane–methacrylate crosslinkers diluted with dichloromethane along with 5 wt %
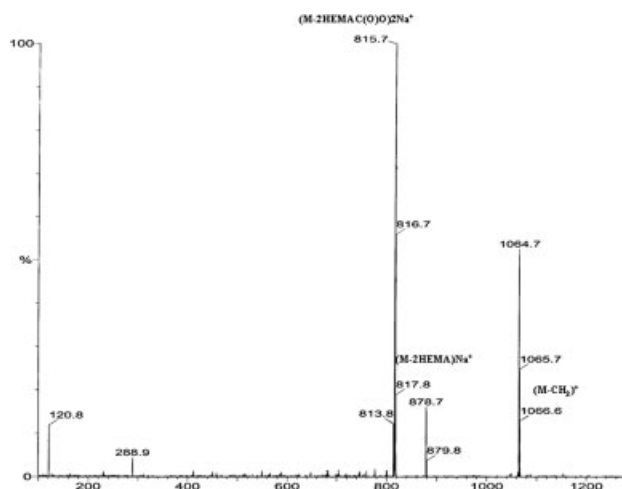
**Figure 3** MALDI-TOF spectra of MCPIH.
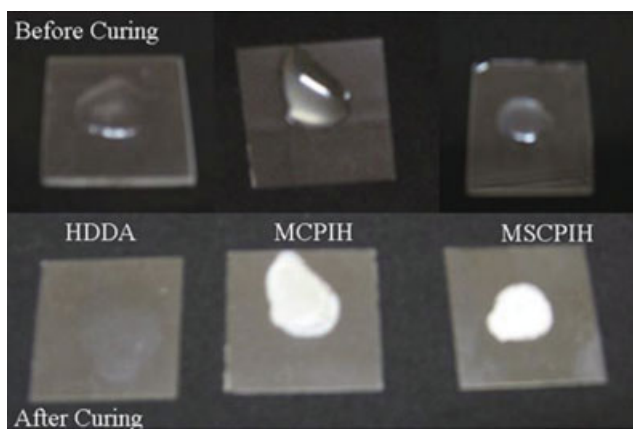
Figure 4 Photographs showing HDDA, MCPIH and MSCPIH in presence of 5 wt % photoinitiator coated on glass substrates before and after 500 s of UV exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

photoinitiator (2,2-diethoxy acetophenone), were subjected to photopolymerization by UV irradiation. The methacrylate/photo initiator mixture was coated on KBr plates with draw-down bars to obtain films $\sim$ 150 µm thick, the IR spectrum of the nonirradiated sample was recorded, and the plate in its holder was subjected to UV exposure. The kinetics of the photoinitiated polymerization of methacrylate double bonds could be monitored through the FTIR peaks at 810/815 cm^{-1} at definite intervals, and the disappearance of the —C=C— peak at 815 cm^{-1} was followed.[30,31] The spectra recorded in the absorbance mode were normalized with the carbonyl peak at approximately 1728/1717 cm^{-1} as the internal standard.[32] A sample of hexanediol diacrylate (HDDA) prepared under similar conditions was used as the standard for comparative studies of the curing kinetics. HDDA has excellent adhesion, high reactivity, and good flexibility, so it is used as one of the components in most commercial curing formulations. Interestingly, upon casting the photoinitiator mixed samples onto KBr plates, the crosslinkers - MCPIH and MSCPIH formed opaque films on the surface within a fraction of a second even without UV irradiation. However, under identical conditions HDDA took more than 500 s of UV irradiation for the formation of peelable films. Figure 4 shows the photographs corresponding to the three samples HDDA, MCPIH, and MSCPIH coated onto glass substrates before and after 500 s of UV exposure. The double-bond content of the uncured formulation was defined as 100%. The degree of conversion (X) was calculated using eq. (1)[32]

$$X = (A_0 - A_t/A_0) \times 100 \qquad (1)$$

Where A_0 is the peak intensity at 810/815 cm^{-1} of the uncured sample with the photoinitiator added

which indicates the unsaturation content and A_t is the corresponding peak intensity after irradiation for time t. The polymerization of the methacrylate double bonds proceeds rapidly upon exposure to the UV radiation of the mercury lamp, with the formation of a tight three-dimensional polymer network. After 500 s of UV irradiation MCPIH formed transparent films, MSCPIH formed brittle films whereas HDDA still remained tacky. Figure 5 presents a comparison of the expanded region of the FTIR spectra, showing the 810 cm^{-1} region of HDDA, MCPIH, and MSCPIH before and after UV irradiation for 500 s. The arrow mark indicates the methacrylate double-bond peak at 815 or 810 cm^{-1}, and the decrease in the intensity of the latter peak was followed as a function of time. Table I gives the extent of conversion for the hydrogen-bonded and nonhydrogen-bonded systems at 815 and 810 cm^{-1}, respectively, and Figure 6 gives the kinetic plot for the same. It clearly shows that there is a higher overall degree of conversion for the hydrogen bonded series than for the nonhydrogen-bonded HDDA. The final overall double bond conversion after 500 s was $\sim$ 13% for HDDA, 84% for MCPIH, and 60% for MSCPIH. Previous reports from our group on UV curing kinetics of telechelic urethane methacrylates based on poly(propylene glycol) (PPG) and tricyclodecane dimethanol had showed that these systems which had the ability to hydrogen bond via the urethane linkage showed a faster crosslinking of their double bonds compared to analogous standards that lacked the hydrogen bonding and had only telechelic methacrylate linkages.[26,27] The observed hydrogen bonding in these urethane systems is the average of both primary and secondary types of NH groups taking part in hydrogen bonding. Additionally, it is
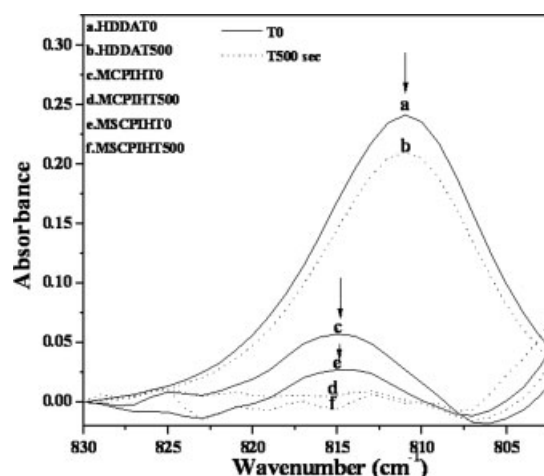
Figure 5 FTIR spectra of (a,b) HDDA, (c,d) MCPIH and (e,f) MSCPIH before (−) and after 500 s (—) of UV irradiation.
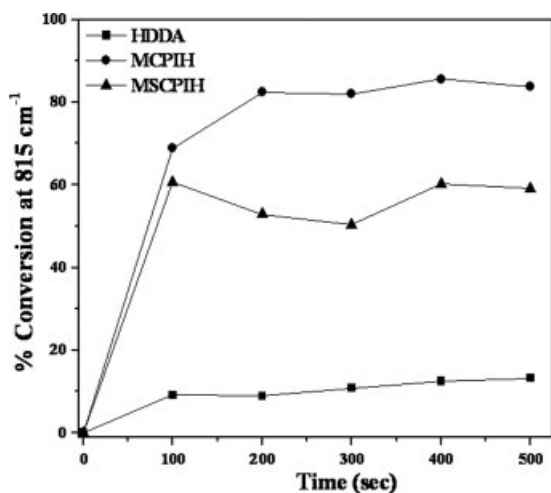
TABLE I
UV Curing Kinetics Data at 25°C for the Hydrogen Bonded and Nonhydrogen Bonded Cross Linkers Obtained by Monitoring the FTIR Peak ~ 815 cm^{-1}

Time (s)	HDDA (811 cm^{-1})	MCPIH (814 cm^{-1})	MSCPIH (815 cm^{-1})
0	–	0	0
100	9	69	61
200	9	82	53
300	11	82	50
400	13	86	60
500	13	84	60

TABLE II
Conversion % of Methacrylic Double Bond at 811 or 813 cm^{-1} after 500 s min of UV Irradiation at Variable Temperatures for HDDA, MCPIH, and MSCPIH

Temperature (°C)	Estimated conversion % (X) after 500 s UV irradiation		
	HDDA 811	MCPIH 813	MSCPIH 813
20	28	72	52
48	20	63	44
58	38	35	72
73	44	53	40
84	57	48	38
105	76	35	37

interesting to note that IPDI itself is a mixture of both cis (z) and trans (E) isomers which further complicates the determination of the extent of hydrogen bonding ability of the different types of urethane units. The overall hydrogen bonding in these telechelic urethane methacrylates results in a preorganization in these systems which brings the double bonds within close proximity leading to faster crosslinking.[23]

Hydrogen bonding

The influence of hydrogen bonding in the UV curing process was further investigated by carrying out the UV curing process at varying temperatures.[33,34] It is expected that at higher temperatures the hydrogen bonding would be broken which should be reflected as a decrease in the curing rates. Samples of HDDA, MCPIH, and MSCPIH were prepared as thin films of ~ 150 μm thickness on KBr plates which were kept on a calibrated hot plate pre heated to each set temperature. At each set temperature, an initial t_0 reading of the 815 cm^{-1} peak was measured using FTIR

and this was assumed as the 100% methacrylate content at that temperature. The samples were then subjected to continuous UV irradiation for 500 s at each set temperature and the final t_{500} reading of the 810/815 cm^{-1} peak was measured using FTIR. Table II gives the estimated conversion values after 500 s of UV irradiation for the three samples HDDA, MCPIH, and MSCPIH at various temperatures. Figure 7 shows the conversion versus temperature plot for the three samples. It can be seen that HDDA has an increasing slope (slope value = 0.6) for the conversion with increase of temperature due to increased activation that typically occurs with increasing temperature. On the other hand, MCPIH (slope value = −0.4) and MSCPIH (slope value = −0.2) showed a decreasing slope with increase of temperature indicating the negative activation associated with decreased strength and/or extent of hydrogen bond at elevated temperature. In the latter case, there is a competing behavior with normal increase in polymerization rates with increasing temperature alongside decrease of polymerization rate

Figure 6 Conversion percent of unsaturated bond for crosslinkers at 815 cm^{-1} at room temperature.
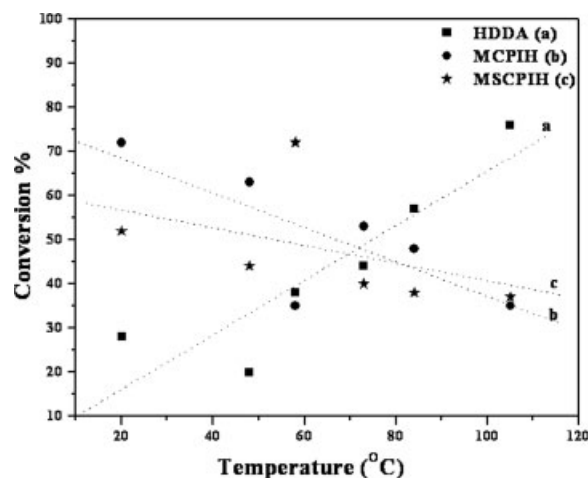
Figure 7 Conversion percent of unsaturated bond at 815 cm^{-1} for (a) HDDA (b) MCPIH and (c) MSCPIH at varied temperature.
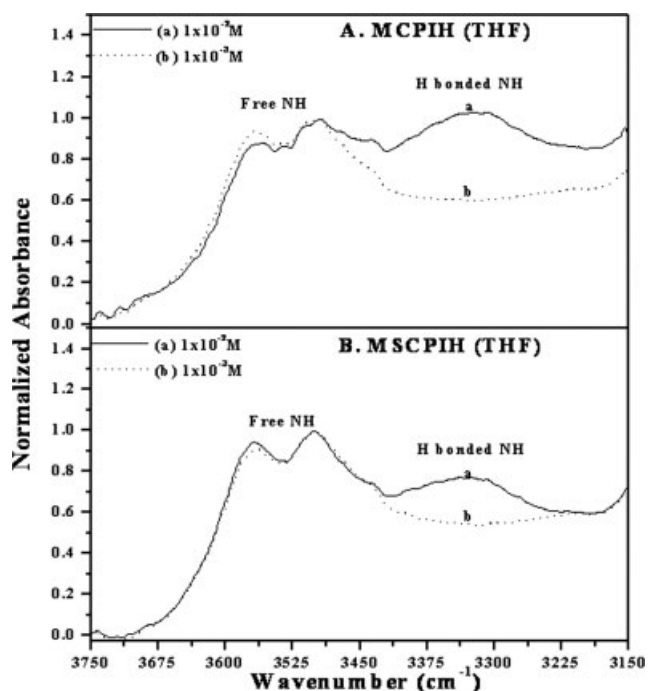
Figure 8 Normalized FTIR spectra of (a) MCPIH and (b) MSCPIH at two different concentrations (straight line $1 \times 10^{-2}M$ and dotted line $1 \times 10^{-3}M$) in THF showing the expanded NH stretching frequencies.

due to reduction in the extent of hydrogen bonding. This indicates that hydrogen bonding does play a major role in the polymerization of these novel crosslinkers.

Comparing the two hydrogen bonded crosslinkers—MCPIH and MSCPIH, the one based on unsaturated cardanol (MCPIH) showed a higher extent of double bond conversion (Fig. 6, 84% Table I). This behavior was reflected in the variable temperature UV curing studies also with the MCPIH showing a higher extent of curing even at the high temperature of 84°C compared to MSCPIH. This is indicative of a higher extent of hydrogen bonding existing in the former compared to the latter. In the variable temperature UV curing studies, MCPIH also exhibited a steeper slope compared to MSCPIH which is a further indication of the high dependence of the curing rate on hydrogen bonding factor.

To gain insight into the different hydrogen bonding tendencies of two otherwise very similar monomers, solution-dependent FTIR measurements were carried out at different concentrations in THF. Figure 8 shows the normalized expanded region of the N—H stretching vibration for MCPIH (A) and MSCPIH (B) in THF at two different concentrations. In both monomers an additional peak appears at lower wavenumbers at high concentration. The two bands at higher wavenumbers (3568 and 3500 cm^{-1}) are assigned to the free antisymmetric and symmet-

ric stretching vibrations of the N—H group in the urethane linkage, respectively.[35,36] The band at lower wavenumber (3327 cm^{-1}) for the higher concentrated solution is assigned to the hydrogen-bonded N—H stretching vibration. For all cases the spectra are normalized with respect to the free NH stretching vibrations. From the spectra at high concentration, the areas under the hydrogen bonded NH peak region and free NH peak region were obtained after deconvolution. The ratio of the hydrogen bonded to free NH was obtained as 12 for MCPIH whereas this value was only 5 in the case of MSCPIH. This gives a quantitative confirmation of the assumption of higher extent of hydrogen bonding in the cardanol-based crosslinker compared to its saturated analogue. It is a rather surprising fact that two similar monomers except for the presence of unsaturation in one of them should show different extents of hydrogen bonding. The effect of such a small structural variation on the molecular packing and self-assembly properties were very beautifully demonstrated in the work reported by George John et al.[18,19] They synthesized glycolipids based on cardanol and its saturated analogue and showed their self-assembly into helical coiled-ribbon structure for the former and twisted nanostructure for the latter. X-ray powder diffraction measurements showed that the cardanol derived glycolipid had a larger d spacing compared to that of the saturated glycolipid. They reasoned that the *cis-cis* double bonds or "kinks" in the former prevents interdigitization and crystallization and the side chain therefore has a fluid-like nature in contrast to the aliphatic side chain crystallization in the saturated glycolipid. In the present example also, the fluid-like nature of the side chain in MCPIH allows for a better preorganization and higher extent of hydrogen bonding leading to a faster curing rate when compared to the more solid crystalline nature of MSCPIH.

Thermal properties

The cured films were subjected to differential scanning calorimetric analysis to obtain the glass transition temperature (T_g) values. T_g data reveals information regarding the physical state of a coating. Figure 9 shows the first cooling cycle of the DSC thermograms of the cured films of (a) MCPIH and (b) MSCPIH and the T_g values were 114 and 106°C, respectively. They showed clear glass transition temperatures with absence of any crystallinity; thus confirming the amorphous nature of the crosslinked network. The T_g of MCPIH system is slightly higher than that of MSCPIH suggesting larger crosslinking density and reduced segmental mobility. The thermal stability of the crosslinked films were determined using thermogravimetric analysis (TGA).
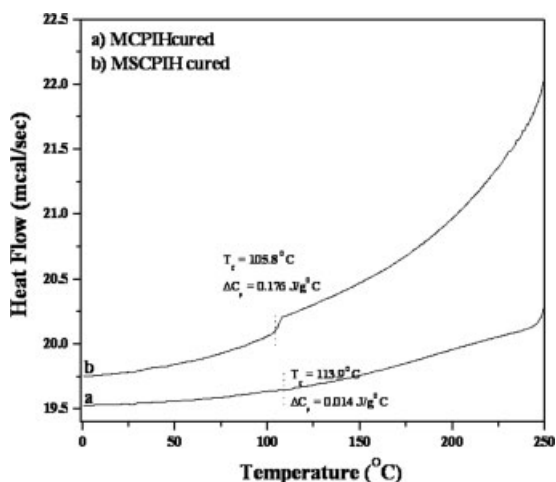
Figure 9 DSC data for the cured samples.

Figure 11 WXRD patterns of crosslinked samples of (a) MSCPIH and (b) MCPIH.

The TGA thermograms of MCPIH and MSCPIH are given in Figure 10. The thermal stability data also indicates a higher crosslinking density for MCPIH in comparison to MSCPIH. Weight loss starts occurring $\sim 180°C$ and the 10 wt % loss temperature was 245 and 232°C for MCPIH and MSCPIH respectively.

The absence of crystallinity in these crosslinked polymer networks was further confirmed by WXRD studies. WXRD patterns were recorded for powdered crosslinked film samples of both MCPIH and MSCPIH and are given in Figure 11. Both samples revealed broad amorphous halo extending from a 2θ range of 10–30° without any peaks of crystallization. This is expected behavior of the hydrogen bond induced hard phase of the polyurethane present in these systems.[10]
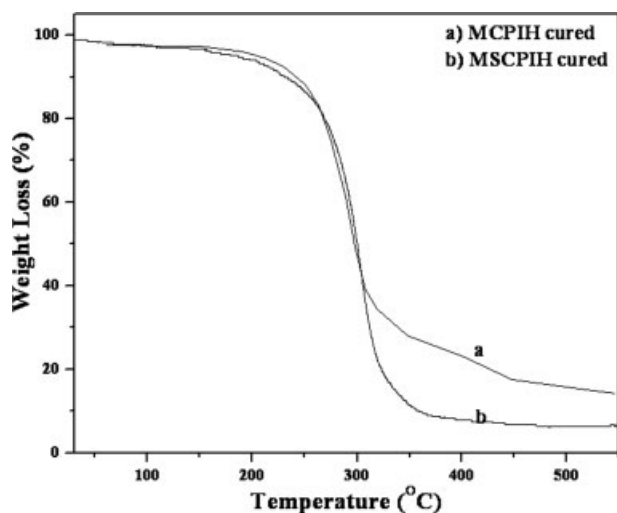
CONCLUSIONS

A new class UV curable telechelic urethane–methacrylate crosslinkers based on the natural resource cardanol was successfully synthesized and characterized. UV irradiation of the resulting telechelic methacrylates in presence of photoinitiators for 500 s resulted in the formation of peelable films when compared to a standard nonhydrogen bonding diacrylate like HDDA, which remained tacky under identical irradiation conditions. The extent of methacrylic double bond conversion upon UV irradiation, which was followed by monitoring the disappearance of the peak $\sim 810/815$ cm^{-1} using FTIR spectroscopy, was found to be higher for systems containing the urethane linkage compared to diacrylates like HDDA. Hydrogen bonding is assumed to play an important role in affecting the rate of polymerization by reducing the termination process by way of reduced polymer radical mobility. These telechelic urethane methacrylates can be used in any coating formulation as fast curing crosslinkers that additionally provides improved mechanical stability to the final coating. The development of these resins based on cardanol reported here offers a new perspective for the utilization of the abundant renewable resources contributing to global sustainability without depletion of scarce resources.

Figure 10 Comparison of TGA thermograms for the cured samples.

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