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Synthesis and Characterization of UV-Curable Poly(dimethylsiloxane) Dimethacrylate

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Summery: This paper presents a new route to the synthesis of UV-curable poly(dimethylsiloxane) dimethacrylate (PDMSDMA). PDMSDMA was essentially prepared by modification of poly(dimethylsiloxane), bis(3-aminopropyl) terminated ($PDMS-NH_2$) with methacrylic anhydride (MAA). The synthesized products were cured under UV in the presence of camphorquinone (CQ) used as a photoinitiator. The chemical structure of PDMSDMA samples was analyzed by FT-IR and ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectrum of PDMSDMA revealed new peaks at 3.20 ppm, corresponding to methylene protons in $-CH_2-NH-$, and 5.25 and 5.65 ppm, corresponding to vinylic protons in $-NH-CO-CCH_3{=}CH_2$. The chemical structure of the cured products and the degree of curing were determined by solid state ^{13}C CP/MAS NMR and FT-IR (Micro-ATR) spectroscopy. Various parameters, such as concentration of methacrylic anhydride, amount of camphorquinone, and curing time, were studied.

Keywords: methacrylic anhydride; poly(dimethylsiloxane)

Introduction

Polydimethylsiloxanes (PDMS) are usually known as silicone or silicone elastomers that have a wide range of applications. Their unique properties, such as good resistance to high temperature, low surface tension and energy, low dielectric constant, high resistance to ozone, and transparence to visible and UV light, were widely recognized.[1–3] In general, PDMS needs crosslinking to satisfy operating requirements. The traditional thermal treatment of PDMS takes much time and energy. In recent years, the photocrosslinking of PDMS functionalized with acrylic acid[4–6] or isocyanatoethylmethacrylate[7] was reported. In this study, poly(dimethylsiloxane) dimethacrylate (PDMSDMA), containing methacrylate groups, was prepared by modification of poly(dimethylsiloxane), bis(3-aminopropyl) terminated ($PDMS-NH_2$) with methacrylic anhydride. These methacrylate-encapped PDMS products were readily subjected to UV curing. The PDMSDMA and its cured products were analyzed by ^{1}H NMR, solid state ^{13}C CP/MAS NMR and FT-IR (Micro-ATR) spectroscopy.

Experimental Part

Materials

Poly(dimethylsiloxane), bis(3-aminopropyl) terminated (Mn ≈ 2500 g/mol) and methacrylic anhydride (MAA) were purchased from Aldrich Chemical Co. Camphorquinone (CQ), a photoinitiator, was supplied by Esstech Company. All reagent-grade chemicals were used as received.

Synthesis of Poly(dimethylsiloxane) Dimethacrylate (PDMSDMA)

Typically, toluene-dissolved $PDMS-NH_2$ and MAA were mixed with certain mole ratios and allowed to react to each other at 110 °C for 4 hr under nitrogen. The product was then cooled to 60 °C, and toluene, unreacted MAA and produced methacrylic acid were afterwards removed under reduc-

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ed pressure. The synthesized PDMSDMA was clear viscous liquid.

Photocrosslinking of PDMSDMA

Varied quantities of CQ were dissolved in a fixed amount of PDMSDMA samples. The samples were UV-cured under filtered blue light (3M ESPE, 420–500 nm) for different curing times, i.e., 30, 45 and 60 min.

Characterization

Structural analysis: The chemical structures of PDMSDMA samples and their starting material, PDMS-NH$_2$, were investigated by using FT-IR (Perkin Elmer System 2000) and ^{1}H NMR (Bruker DPX-300) spectrometers. The percentage of conversion of PDMS-NH$_2$ to PDMSDMA was calculated from the peak areas of the remaining methylene protons (NH$_2$–CH_2–, at 2.65 ppm) and newly produced methylene protons adjacent to a secondary amine (–CH_2–NH–, at 3.20 ppm).

Degree of curing: Double bond conversion was determined by an FT-IR (Micro-ATR) spectrometer (Perkin Elmer Spectrum Spotlight FT-IR Imaging System). The degree of curing or double bond conversion was calculated based on the ratio of peak areas of –*CO*NH– and –CH$_3$*C*=*C*H$_2$ stretching bands at 1656 and 1625 cm^{-1}, respectively.

Results and Discussion

The reaction scheme for the synthesis of a UV-curable PDMSDMA sample is shown in Figure 1. The synthesized product was encapped with methacrylate groups at both ends.

The chemical structure of PDMSDMA samples was verified by a ^{1}H NMR spectroscopic technique. The spectrum of PDMS-NH$_2$ shown in Figure 2(a) possessed the resonance peaks at 0.08, 0.53, 1.46 and 2.67 ppm, belonging to the protons of Si–CH_3, Si–CH_2, –CH$_2$–CH_2–CH$_2$– and –CH_2–NH$_2$, respectively. The structural change was observed after PDMS-NH$_2$ was reacted with MAA; new peaks at 3.20 ppm, corresponding to methylene protons adjacent to a secondary amine (–CH_2–NH–), and 5.25 and 5.65 ppm, corresponding to vinylic protons in –NH–CO–CCH$_3$=CH_2, arose as shown in Figure 2(b–d). The conversion of –NH$_2$ groups to methacrylate groups was obviously affected by the amount of MAA used. In Figure 2(d), the resonance peak of methylene protons attached to a primary amine (–CH_2–NH$_2$) at 2.67 ppm absolutely vanished when a highly excess amount of MAA was employed.

The %conversion was calculated based on the ratio of peak intensities of methylene protons attached to a secondary amine (–CH_2–NH–) at 3.20 ppm and methylene protons attached to a primary amine (–CH_2–NH$_2$) at 2.67 ppm. The determined values are reported in Table 1. The obtained conversion seemed to be greater than the theoretical values. The actual molecular weight of PDMS-NH$_2$ might be higher than the number indicated. As a

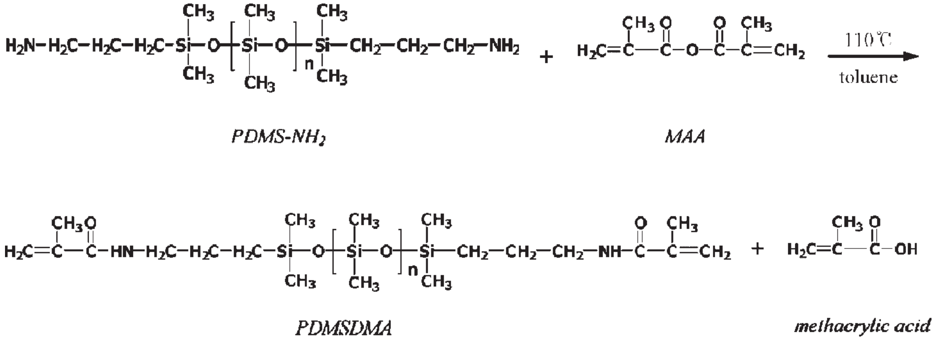

Figure 1.
Synthesis of UV-curable PDMSDMA.

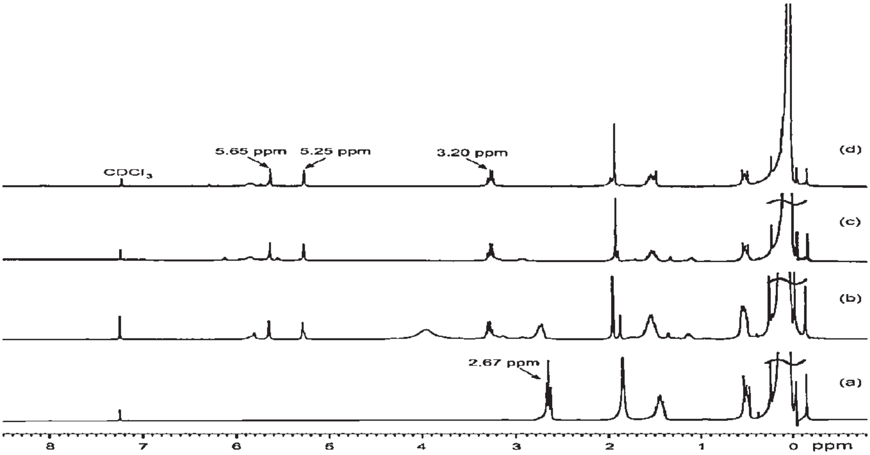

Figure 2.
The ^{1}H NMR spectra of (a) PDMS-NH$_2$ and (b-d) PDMSDMA samples prepared by mole ratios of –NH$_2$ in PDMS-NH$_2$ to MAA = 4:1, 2:1 and 1:1, respectively.

consequence, the actual –NH$_2$ groups present in the reaction were initially over estimated, leading to the incorrectly stated mole ratios of –NH$_2$ groups in PDMS-NH$_2$ to MAA. However, it was noted that the greater the mole ratio of –NH$_2$ end groups in PDMS-NH$_2$ to MAA used, the lower the percentage of conversion achieved.

The chemical structure of the UV-cured PDMSDMA samples was essentially determined by solid state ^{13}C CP/MAS NMR spectroscopy. In the ^{13}C NMR spectrum of PDMSDMA demonstrated in Figure 3(a), four major absorption peaks were observed. They belonged to vinylic carbons in $-NH-CO-CH_3C{=}CH_2$ at 119 and 140 ppm, carbonyl carbon in $-CONH-$ at 168 ppm, and methylene carbon in $-CH_2-NH-$ at $\approx$43 ppm. After curing, a new resonance peak at 45.7 ppm, corresponding to the saturated methylene carbon in the methacrylate groups, emerged as revealed in the spectrum in Figure 3(b). The degree of curing or double bond conversion was evaluated by FT-IR (Micro-ATR) spectroscopy. Figure 4 shows the overlaid FT-IR spectra of uncured and cured PDMSDMA samples. The characteristic absorption peaks at 1656 and 1625 cm^{-1} corresponded to an amide I band ($-CONH-$) and a carbon-carbon double bond ($-NH-CO-CH_3C{=}CH_2$) stretching band, respectively. In Figure 4(b), the peak intensity at 1625 cm^{-1} nearly disappeared after irradiation, indicating that the degree of cross-linking was enormous.

The degree of curing was calculated based on the ratio of peak areas of an amide I band and a carbon-carbon double bond stretching band at 1656 and 1625 cm^{-1}, respectively. The determined values are reported in Table 2. It was found that the double bond conversion was directly dependent on the quantity of CQ used. A very high conversion (90%) was reached when 3 wt% CQ was used. On the other hand, the number was reduced to 31% when only 1 wt% CQ was employed. The

Table 1.
Effect of MAA concentration on %conversion of synthesis of PDMSDMA samples.

Run	Sample Code	Mole Ratio		%Conversion
		–NH$_2$ groups in PDMS-NH$_2$	MAA	
1	PDMSDMA1	1	1	100
2	PDMSDMA2	2	1	85
3	PDMSDMA3	4	1	47

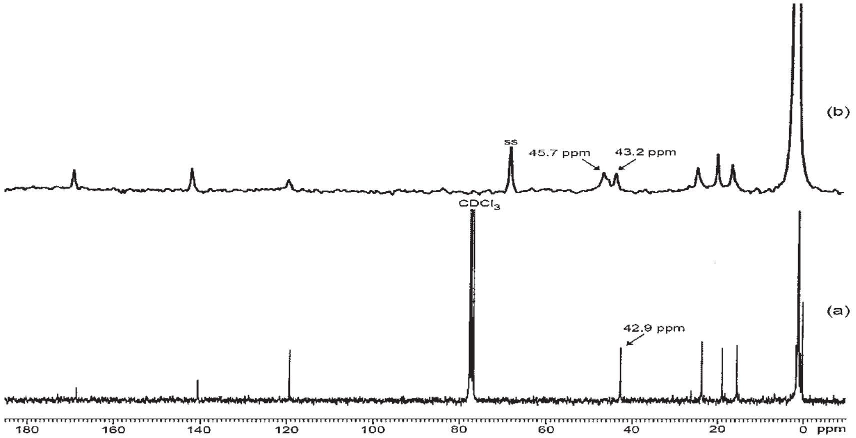

Figure 3.
The ^{13}C NMR spectra of (a) PDMSDMA1 and (b) PDMSDMA1 cured by 1 wt% CQ.

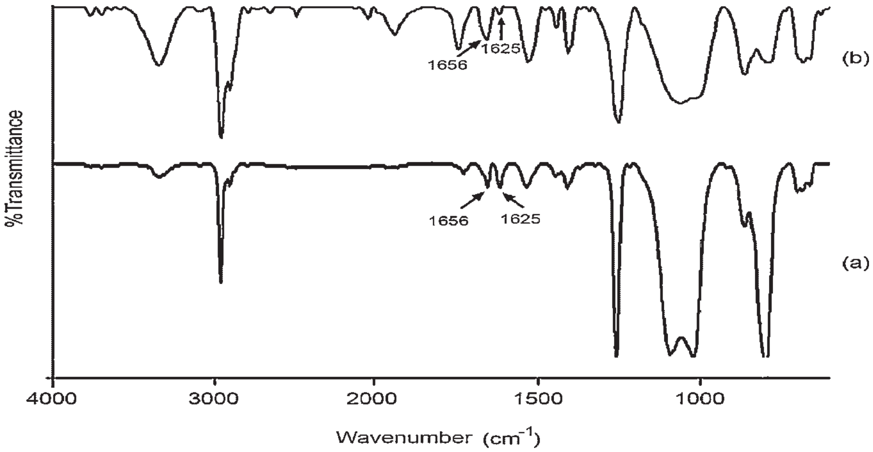

Figure 4.
The FT-IR spectra of (a) PDMSDMA1 and (b) PDMSDMA1 cured by 3 wt% CQ.

curing time did not alter the degree of curing much. When PDMSDMA samples were cured with 3 wt% CQ for different curing times, i.e., 30, 45 or 60 min, the degree of curing fell in the range of 82–90.

Table 2.
Effect of CQ concentration on degree of curing of PDMSDMA*.

Run	Sample Code	CQ (wt%)	Degree of Curing
1	PDMSDMACQ1	3	90
2	PDMSDMACQ2	1	31

curing was 30 min.

Conclusion

The UV-curable poly(dimethylsiloxane) dimethacrylate (PDMSDMA) samples were successfully synthesized via a reaction between PDMS-NH$_2$ and methacrylic anhydride (MAA). The optimal reaction condition to completely convert –NH$_2$ groups to methacrylate groups was to use a 1:1 strochiometric ratio of amine to methacrylic anhydride. The PDMSDMA samples were readily cured with CQ under UV light. The quantity of CQ used markedly governed the double bond conversion. The effect of the curing time on the degree of curing was, however, insignificant.

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