

## Supporting Information

**The role of molecular structure on impact resistance and bending strength of photocured urethane-dimethacrylate polymer networks**

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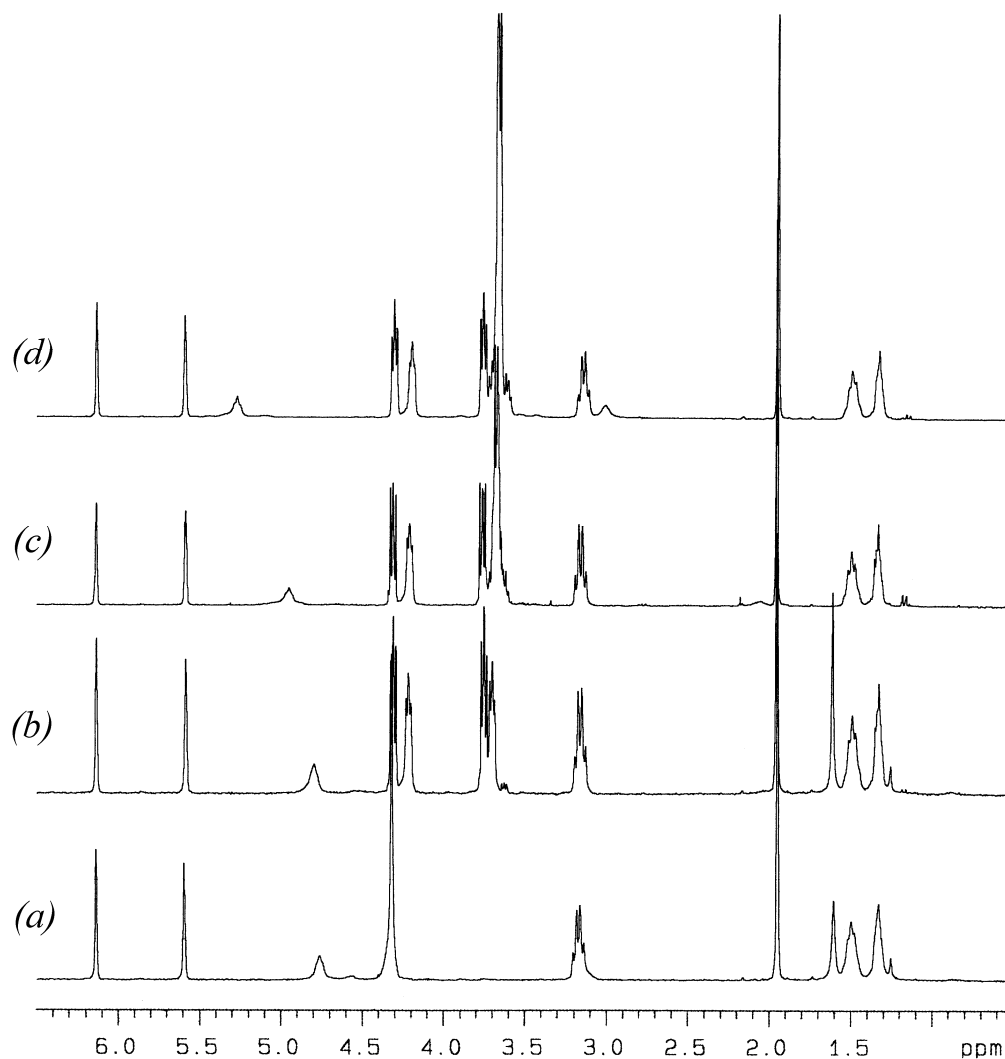
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Figure S1. The  $^1\text{H}$  NMR spectra of the OEGMMA/HMDI series: (a) HEMA/HMDI, (b) DEGMMA/HMDI, (c) TEGMMA/HMDI, (d) TTEGMMA/HMDI.



$\delta=1.32$  ppm and  $\delta=1.49$  ppm (2m, 8H,  $-\text{CH}_2-$ ),  $\delta=1.95$  ppm (s, 6H,  $\text{CH}_3-\text{C}$ ),  $\delta=3.15$  ppm (q, 4H,  $-\text{OCONHCH}_2-$ ),

(a)  $\delta=4.32$  ppm (s, 8H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ),

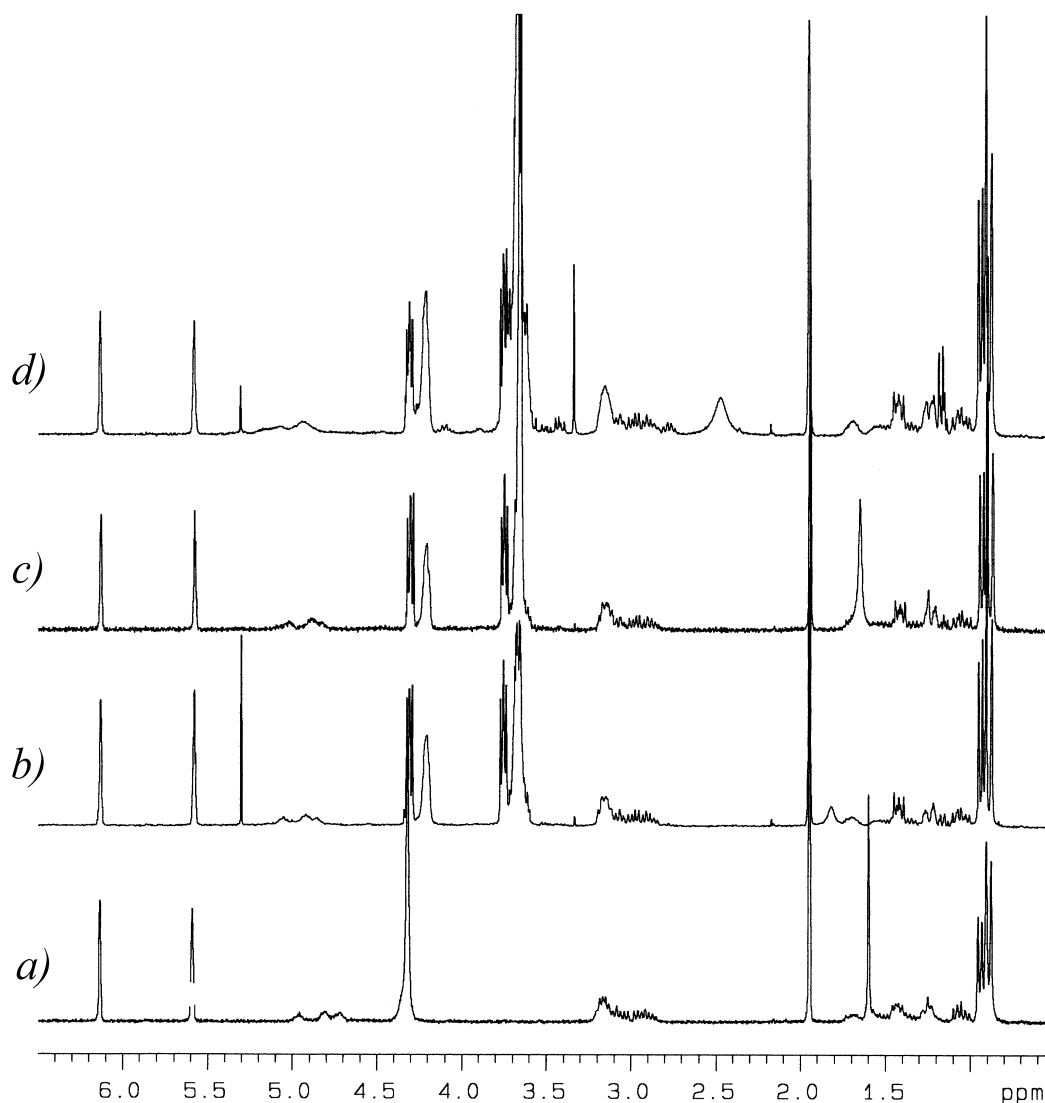
(b)  $\delta=3.70$  and  $3.77$  ppm (2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(c)  $\delta=3.70$  and  $3.77$  ppm (1s, 8H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(d)  $\delta=3.70$  and  $3.77$  ppm (1s, 16H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

$\delta=4.85$ - $5.25$  ppm (t, 2H,  $-\text{NHCOO}-$ ),  $\delta=5.59$  and  $\delta=6.14$  (2s, 4H,  $\text{CH}_2=$ ).

Figure S2. The  $^1\text{H}$  NMR spectra of the OEGMMA/TMDI series: (a) HEMA/TMDI, (b) DEGMMMA/TMDI, (c) TEGMMA/TMDI, (d) TTEGMMA/TMDI.



$\delta=0.91$  ppm (q, 9H,  $-\text{CH}_3-$ ),  $\delta=0.98-1.80$  ppm (m, 5H,  $-\text{CH}_2-$ ,  $-\text{CH}<$ ),  $\delta=1.95$  ppm (s, 6H,  $\text{CH}_3-$ ),  $\delta=2.70-3.22$  ppm (q, 4H,  $-\text{OCONHCH}_2-$ ),

(a)  $\delta=4.32$  ppm (s, 8H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ),

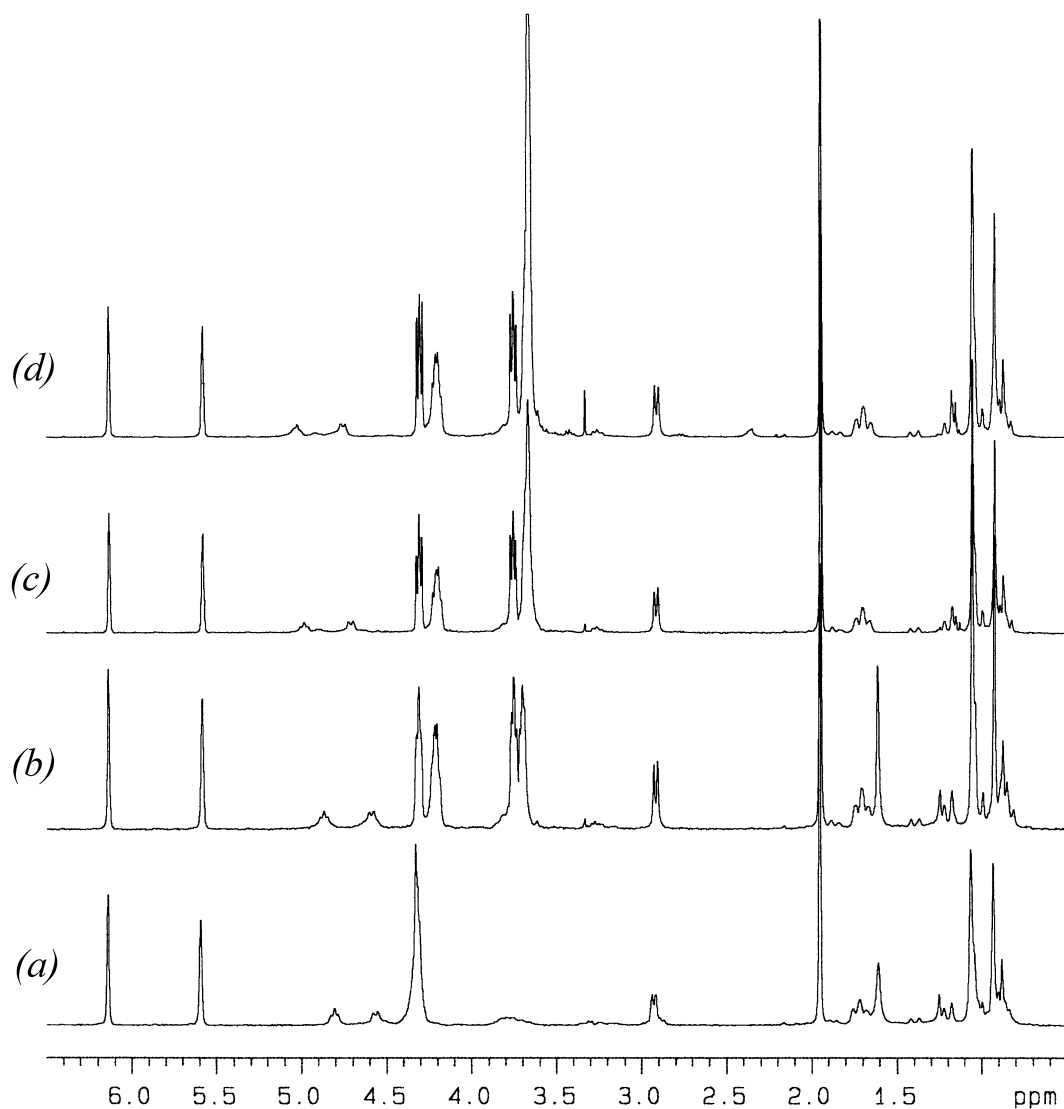
(b)  $\delta=3.70$  and  $3.77$  ppm (2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(c)  $\delta=3.70$  and  $3.77$  ppm (1s, 8H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(d)  $\delta=3.70$  and  $3.77$  ppm (1s, 16H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

$\delta=4.71$  and  $4.95$  ppm (2t, 2H,  $-\text{NHCOO}-$ ),  $\delta=5.59$  and  $\delta=6.14$  (2s, 4H,  $\text{CH}_2=$ ).

Figure S3. The  $^1\text{H}$  NMR spectra of the OEGMMA/IPDI series: (a) HEMA/IPDI, (b) DEGMMA/IPDI, (c) TEGMMA/IPDI, (d) TTEGMMA/IPDI.



$\delta=0.8-1.9$  ppm (m, 15H,  $-\text{CH}_2-$ ,  $-\text{CH}_3$ ),  $\delta=1.95$  ppm (s, 6H,  $\text{CH}_3-$ ),  $\delta=2.9-3.9$  ppm (m, 3H,  $-\text{HNCH}_2-$ ,  $-\text{HNCH}_2<$ ),

(a)  $\delta=4.32$  ppm (s, 8H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ),

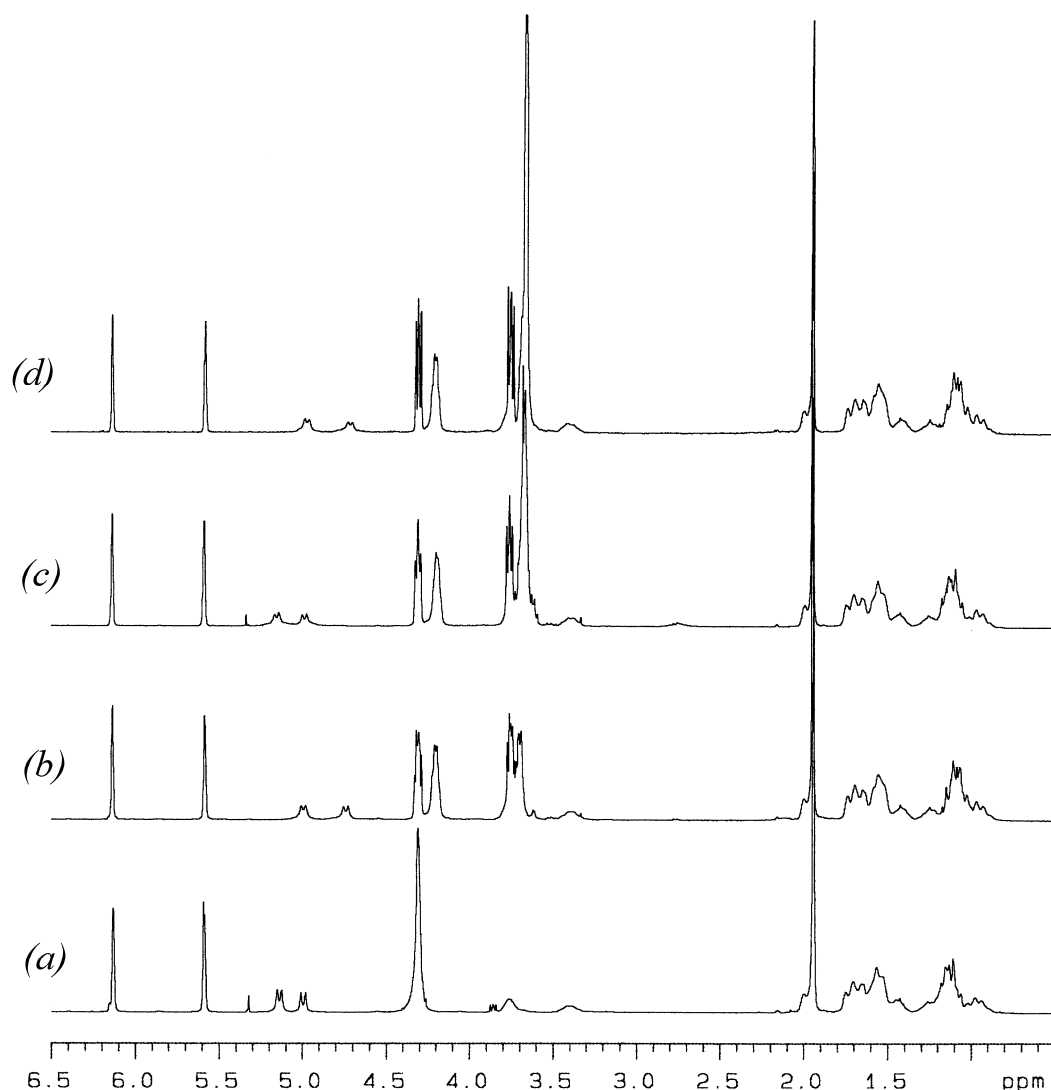
(b)  $\delta=3.70$  and  $3.77$  ppm (2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(c)  $\delta=3.70$  and  $3.77$  ppm (1s, 8H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(d)  $\delta=3.70$  and  $3.77$  ppm (1s, 16H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

$\delta=4.60$  and  $4.90$  ppm (t, d, 2H,  $-\text{NHCOO}-$ ),  $\delta=5.59$  and  $\delta=6.14$  (2s, 4H,  $\text{CH}_2=$ ).

Figure S4. The  $^1\text{H}$  NMR spectra of the OEGMMA/CHMDI series: (a) HEMA/CHMDI, (b) DEGMMA/CHMDI, (c) TEGMMA/CHMDI, (d) TTEGMMA/CHMDI.



$\delta=0.8-2.1$  ppm (m, 20H,  $-\text{CH}_2-$ ,  $>\text{CH}-$ ),  $\delta=1.95$  ppm (s, 6H,  $\text{CH}_3-$ ),  $\delta=3.4$  ppm and  $\delta=3.78$  ppm (m, t, 2H,  $>\text{CH}-\text{NH}-$ ),

(a)  $\delta=4.32$  ppm (s, 8H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ),

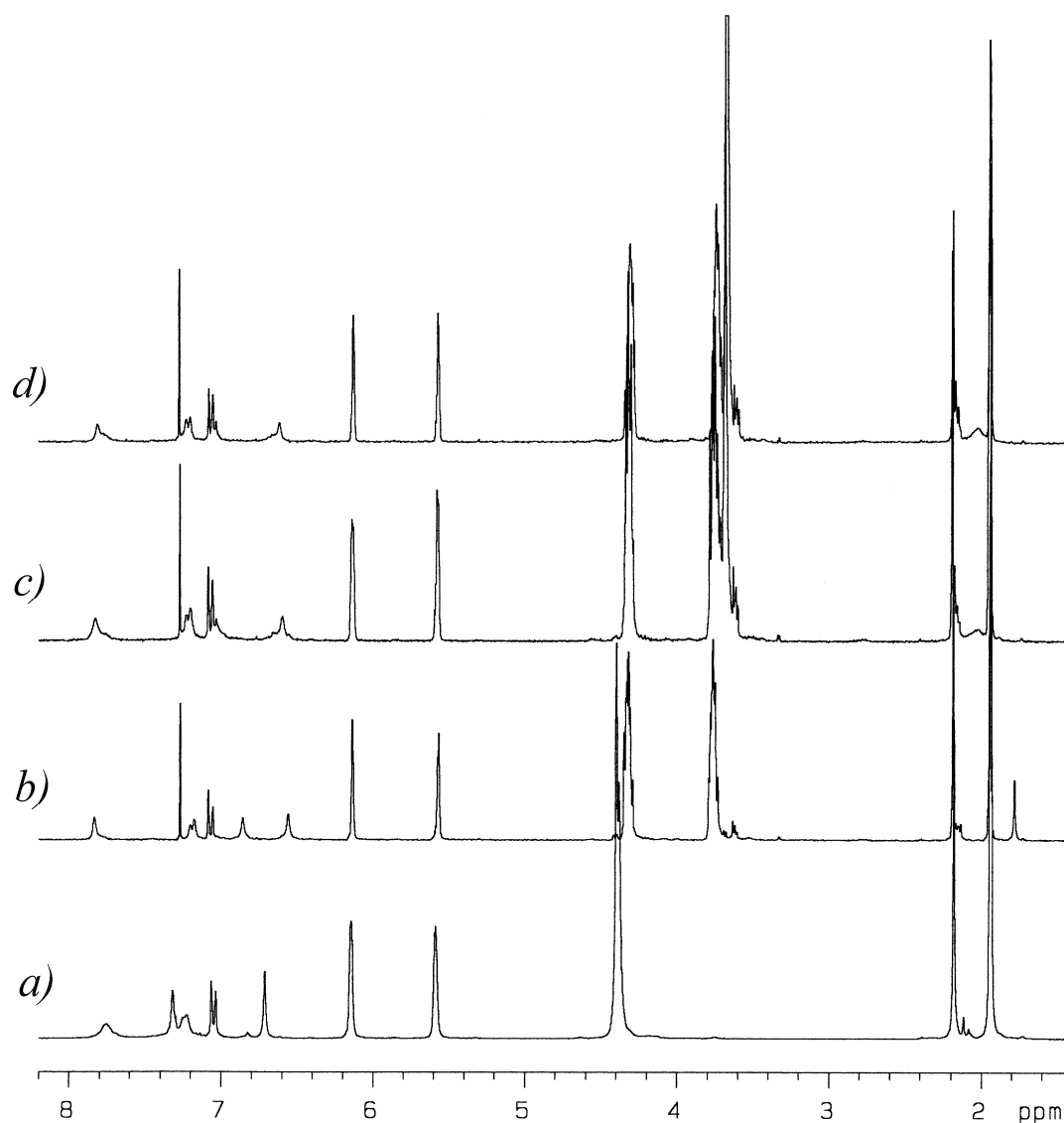
(b)  $\delta=3.70$  and  $3.77$  ppm (2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(c)  $\delta=3.70$  and  $3.77$  ppm (1s, 8H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(d)  $\delta=3.70$  and  $3.77$  ppm (1s, 16H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

$\delta=4.96$  and  $5.15$  ppm (2d, 2H,  $-\text{NHCOO}-$ ),  $\delta=5.59$  and  $\delta=6.14$  (2s, 4H,  $\text{CH}_2=$ ).

Figure S5. The  $^1\text{H}$  NMR spectra of the OEGMMA/TDI series: (a) HEMA/TDI, (b) DEGMMA/TDI, (c) TEGMMA/TDI, (d) TTEGMMA/TDI.



$\delta=1.95$  ppm (s, 6H,  $\text{CH}_3-$ ),  $\delta=2.20$  ppm (s, 3H,  $\text{CH}_3-\text{Ar}$ ),

(a)  $\delta=4.4$  ppm (s, 8H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ),

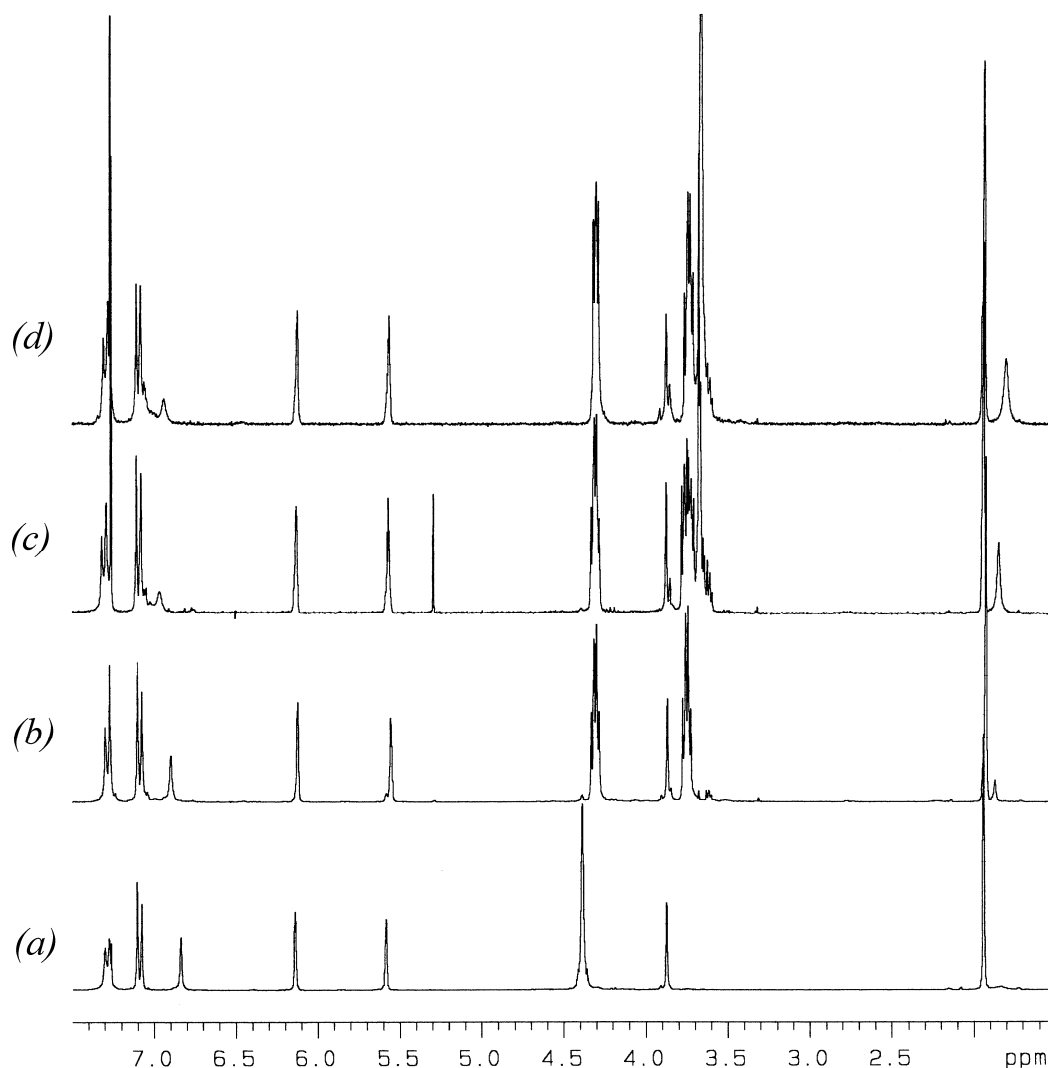
(b)  $\delta=3.70$  and  $3.77$  ppm (2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(c)  $\delta=3.70$  and  $3.77$  ppm (1s, 8H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(d)  $\delta=3.70$  and  $3.77$  ppm (1s, 16H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

$\delta=5.59$  and  $\delta=6.14$  (2s, 4H,  $\text{CH}_2=$ ),  $\delta=6.95$  and  $7.76$  ppm (2s, 2H,  $-\text{NHCOO}-$ ),  $\delta=6.80$  ppm (s, 1H,  $\text{C}(3)_{\text{ar}}$ ,  $-\text{CH}=\text{}$ ) and  $\delta=7.24$  ppm (d, 1H,  $\text{C}(5)_{\text{ar}}$ ,  $-\text{CH}=\text{}$ ),  $7.05$  ppm (d, 1H,  $\text{C}(6)_{\text{ar}}$ ,  $-\text{CH}=\text{}$ ).

Figure S6. The  $^1\text{H}$  NMR spectra of the OEGMMA/MDI series: (a) HEMA/MDI, (b) DEGMMMA/MDI, (c) TEGMMA/MDI, (d) TTEGMMA/MDI.



$\delta=1.95$  ppm (s, 6H,  $\text{CH}_3-$ ),  $\delta=3.87$  ppm (s, 2H,  $\text{Ar-CH}_2\text{-Ar}$ ),

(a)  $\delta=4.4$  ppm (s, 8H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ),

(b)  $\delta=3.70$  and  $3.77$  ppm (2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(c)  $\delta=3.70$  and  $3.77$  ppm (1s, 8H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

(d)  $\delta=3.70$  and  $3.77$  ppm (1s, 16H and 2m, 8H,  $-\text{CH}_2\text{O}-$ ),  $\delta=4.21$  ppm (m, 4H,  $-\text{CH}_2\text{OCONH}-$ ),  $\delta=4.31$  ppm (m, 4H,  $-\text{CH}_2\text{OCO}-$ ),

$\delta=5.59$  and  $\delta=6.14$  (2s, 4H,  $\text{CH}_2=$ ),  $\delta=6.97$  ppm (s, 2H,  $-\text{NHCOO}-$ ),  $\delta=7.08$  ppm and  $\delta=7.30$  ppm (2d, 8H,  $\text{C}(2,2',6,6')_{\text{ar}}$  and  $\text{C}(3,3',5,5')_{\text{ar}}$ ,  $-\text{CH}=\text{}$ ),  $7.05$  ppm (d, 1H,  $\text{C}(6)_{\text{ar}}$ ,  $-\text{CH}=\text{}$ ).

Figure S7. The exemplary FTIR spectra, showing the peak intensity decrease resulting from the polymerization of double bonds: HEMA/TDI (a), DEGMMA/MDI (b), TEGMMA/IPDI (c), and TTEGMMA/HMDI (d) (black—the monomer, gray—the polymer).

