Multifunctional Linear Methacrylate Copolymer Polyenes Having Pendant Vinyl Groups: Synthesis and Photoinduced Thiol–Ene Crosslinking Polyaddition

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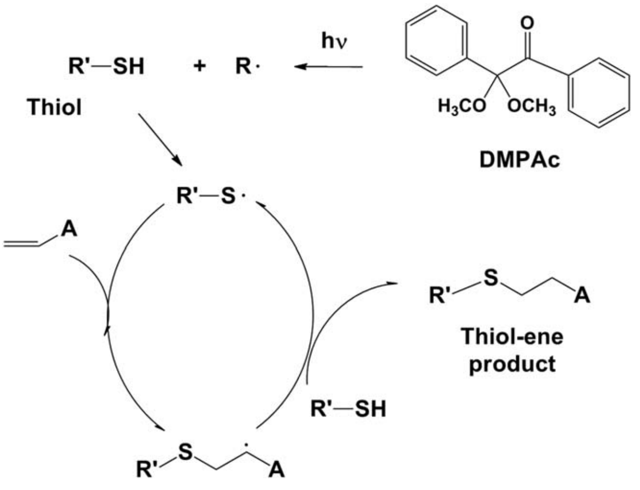
ABSTRACT: UV-induced thiol-ene crosslinked films composed of linear methacrylate copolymers having pendant enes (MCPenes) are reported. An approach involving a combination of controlled radical polymerization to synthesize well-controlled pendant hydroxyl containing copolymers (MCP_{OH}s) with the following facile carbodiimide coupling of the formed MCP_{OH}s with enes allows for the synthesis of well-controlled MCPenes with narrow molecular weight distribution. The density of the pendant enes in MCPenes are easily modulated by varying monomer ratios in the feed. Under UV irradiation, the resulting MCPenes undergo thiol-ene polyaddition reactions with polythiols to form crosslinked films with a uniform network. The results from thermal and mechanical analysis suggest these properties are tuned by adjusting the densities of pendant enes in MCPenes and the amount of thiols in the reactive mixtures. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 572–581

KEYWORDS: atom transfer radical polymerization (ATRP); films; photopolymerization; viscoelastic properties; vesicles

INTRODUCTION Photoinduced thiol-ene reaction is a well-defined ″click-type″ reaction that is highly selective, simple, and orthogonal, resulting in quantitative conversion with a high yield under mild conditions.[1–4] This click reaction involves thiols having relatively weak sulfur-hydrogen bonds and enes having reactive carbon-carbon double bonds. As can be observed in Scheme 1, free radical species (R•), generated upon photolysis of a photoinitiator under UV irradiation, abstracts the hydrogen from thiols (R′-SH), resulting in the corresponding thiyl radicals (R′-S•). This reactive radical can then be added to enes, followed by termination, to yield thiol-ene products with the formation of new sulfide bonds.[5,6] This unique chemistry has been utilized to modify multifunctional polymers and nanostructured materials.[7,8] Specifically, it has been investigated for the synthesis of multifunctional crosslinked nanomaterials to afford hydrogels,[9,10] inorganic-polymer hybrids,[11,12] and soft lithographic materials.[13–15] These engineered materials may find useful applications for optical, biomedical, and sensing fields.[16–19]

Furthermore, the UV-induced thiol-ene process has been explored in the development of crosslinked surface coatings exhibiting rapid cure, uniform network, and tunable mechanical properties. For example, a thiol-ene reactive mixture consisting of a dendritic Boltorn-ene and a four-arm star poly(ethylene glycol)-functionalized tetrathiol was examined for the formation of a crosslinked network exhibiting antibiofouling.[20] Most examples of thiol-enes for surface coating applications utilize small, hyperbranched, or dendric thiols or enes.[21–25] We have recently focused on thiol-ene photocrosslinked network films based on linear or branched, high molecular weight methacrylate copolymers (MCPs) having pendant sulfhydryl (-SH) groups or pendant carbon-carbon double bonds. This new approach enables to tune the balance of rigidity, determined by the carbon-carbon (C—C) single bonds in the polymethacrylate main chains, and flexibility, influenced by the new sulfide (—S—) bonds as crosslinks in crosslinked films. Moreover, additional typical advantages include the possibility of a broad selection of methacrylate monomers to modulate thermal and mechanical properties of crosslinked networks, easy control of crosslinking densities by varying the number of pendant SH or enes, and formation of a uniform network by employing

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Photoinduced thiol-ene radical addition reaction.

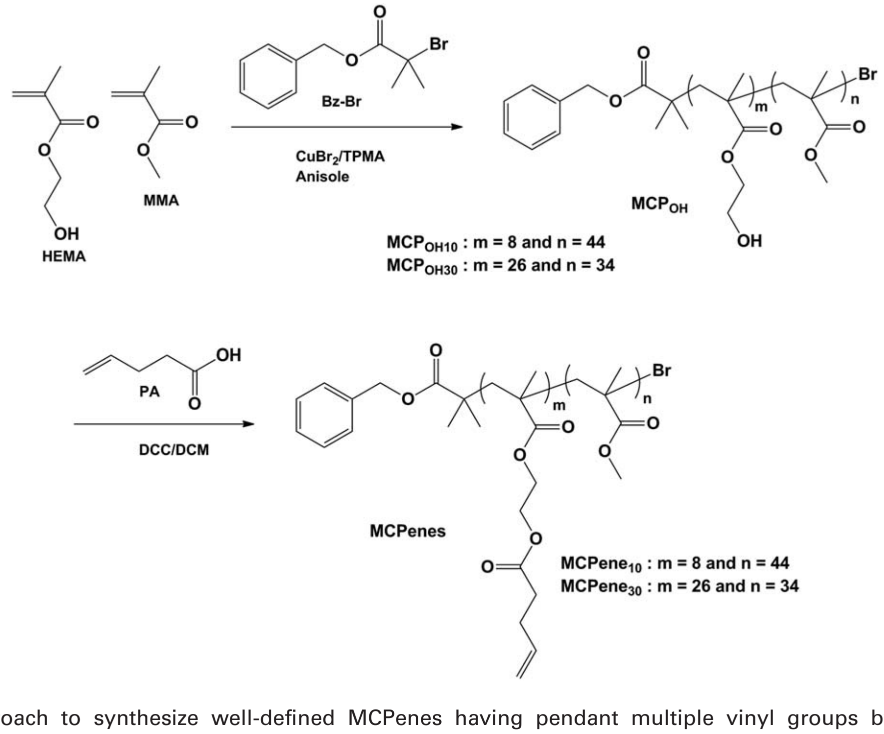
controlled radical polymerization methods, compared with their counterparts of free radical polymerization methods.[26,27] These unique properties can promote the use of new thiol-ene photo-crosslinked network films based on MCPs for high performance coating materials. As a proof of concept, we have reported the synthesis of linear MCPs having pendant SH groups (MCP_{SH}s) by a combination of well-defined atom transfer radical polymerization (ATRP)[28] and disulfide-thiol reductive chemistry.[29,30] The resulting MCP_{SH}s were evaluated with a tetraacrylate as a model ene for UV-induced thiol-ene polyaddition, yielding rapid formation of crosslinked films with uniform network and enhanced mechanical properties.[31]

In this work, we investigated the synthesis and UV-irradiated thiol-ene polyaddition of linear MCPs having pendant vinyl groups (MCPenes). As illustrated in Scheme 2, our approach to prepare well-controlled MCPenes involves the synthesis of the precursors of well-defined MCPs having pendant hydroxyl (OH) groups by ATRP, followed by postmodification of OH groups with 4-pentenoic acid (PA) using a facile carbodiimide coupling reaction. Varying the feed ratios of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) ultimately resulted in the synthesis of MCPenes with differing densities of pendant vinyl groups. With various polythiols, model kinetic studies, using PA as a monoene and formation of crosslinked networks using MCPenes as a multi-ene, were studied to better understand photoinduced thiol-ene addition reactions. Furthermore, the resulting thiol-ene crosslinked films, based on linear MCPenes, were analyzed for thermal and real-time viscoelastic properties.

EXPERIMENTAL

Instrumentation and Analyses

^{1}H-NMR spectra were recorded using a 500 MHz Varian spectrometer. The $CDCl_3$ singlet at 7.26 ppm was selected as the reference standard. Spectral features are tabulated in the following order: chemical shift (ppm); multiplicity (s—singlet, d—doublet, t—triplet, m—multiplet); number of protons; position of protons. Monomer conversion was determined using ^{1}H-NMR for aliquots taken during polymerization. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC). An Agilent GPC was equipped with a 1260 Infinity



SCHEME 2 Our approach to synthesize well-defined MCPenes having pendant multiple vinyl groups by postmodification of MCP_{OH}s having pendant OH groups synthesized by ATRP with PA using a facile carbodiimide coupling reaction.

Isocratic Pump and a RI detector. Two Agilent PLgel mixed-C and mixed-D columns were used with DMF containing 0.1 mol % LiBr at 50 °C at a flow rate of 1.0 mL/min. Linear poly(methyl methacrylate) (PMMA) standards from Fluka were used for calibration. Aliquots of polymer samples were dissolved in DMF/LiBr. The clear solutions were filtered using a 0.25 μm PTFE filter to remove any solvent-insoluble species. A drop of anisole was added as a flow rate marker.

Differential Scanning Calorimetry (DSC) Analysis

Thermal properties including glass transition temperature (T_g) of polymers were measured with a TA Instrument, DSC Q20 differential scanning calorimeter. Polymer samples were dried under vacuum for 24 hrs at room temperature to remove residual solvents. Temperature range was from −70 to 200 °C with heating and cooling cycles conducted at a rate of 10 °C/min (cycles: cool to −70 °C, heat up to 200 °C (first run), cool to −70 °C, heat up to 200 °C (2nd run), and cool to 25 °C). The T_g values were determined from the second heating run.

Materials

Benzyl alcohol (BA, >99.0%), α-bromoisobutyryl bromide (Br-iBuBr, 98%), triethylamine (Et_3N, >99.9%), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 95%), copper(II) bromide ($CuBr_2$, >99.99%), ethanethiol (MonoSH, >97%), trimethylolpropane *tris*(3-mercaptopropionate) (TriSH, >95%), pentaerythritol tetrakis(3-mercaptopropionate) (TetraSH, >95%), 2,2-dimethoxy-2-phenylacetophenone (DMPAc, 99%) as a photoinitiator, *N,N′*-dicyclohexylcarbodiimide (DCC, 99%), 4-(dimethylamino) pyridine (DMAP, >99%), 4-pentenoic acid (PA, 97%) were purchased from Aldrich and used as received. Methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) from Aldrich were purified by passing them through a column filled with basic alumina to remove inhibitors. *Tris*(2-pyridylmethyl)-amine (TPMA) was synthesized according to literature procedure.[32]

Synthesis of Benzyl α-Bromoisobutyrate (Bz-Br)

A clear solution of Br-iBuBr (19 g, 83 mmol) in THF (50 mL) was added drop-wise to a solution consisting of BA (6.0 g, 55 mmol), Et_3N (6.7 g, 67 mmol), and THF (250 mL) in ice bath for 30 min. The resulting mixture was stirred at room temperature for 12 hrs. The solids formed as by-products were removed by vacuum filtration and the organic solvents were removed using rotary evaporation. The resulting mixture was dissolved in ethyl acetate, and washed with 0.1 M aqueous HCl solution (50 mL), followed by saturated aqueous $NaHCO_3$ solution (50 mL), three times. The solution was dried over sodium sulfate and organic solvents were removed by rotary evaporation. The product was purified by silica column chromatography with a mixture of ethyl acetate/hexane (1/9 v/v). The product was collected as the first of a total of two bands from a silica gel column. Yield = 2.5 g (17%). R_f = 0.55 on silica (1/9 ethyl acetate/hexane). ^{1}H-NMR ($CDCl_3$, ppm) 7.36 (m, 5H, C_6H_5-), 5.22 (s, 2H, -CH_2-), 1.94 (s, 6H, -$(CH_3)_2$). ^{13}C-NMR ($CDCl_3$, ppm) 171.5, 135.4, 128.6, 128.3, 127.9, 127.9, 67.6, 55.7, 30.8.

Synthesis of MCP_{OH}s by ATRP

For the synthesis of well-defined MCP_{OH10}, as an example, MMA (6.0 g, 60 mmol), HEMA (0.87 g, 6.7 mmol), TPMA (7.7 mg, 27 μmol), $CuBr_2$ (3.0 mg, 13 μmol), and anisole (21 mL) were mixed in a 50 mL Schlenk flask. The mixture was deoxygenated by purging under nitrogen for 1 hr and placed in an oil bath at 60 °C. A nitrogen-prepurged solution of $Sn(Oct)_2$ (54 mg, 0.13 mmol) in anisole (0.5 g) was injected into the Schlenk flask to initiate polymerization. Polymerization was stopped after 4 hrs by cooling the reaction vessel in an ice bath and exposing the contents to air. For purification, the polymer solutions were diluted with THF and then passed through a basic alumina column to remove the copper complex. The residues were precipitated from hexane three times and then dried under vacuum at room temperature for 18 hrs. Similar procedure was applied to synthesize MCP_{OH30}, except for the use of MMA (6.0 g, 60 mmol), HEMA (3.3 g, 26 mmol), TPMA (9.9 mg, 34 μmol), $CuBr_2$ (3.8 mg, 17 μmol), anisole (28 mL), and $Sn(Oct)_2$ (69 mg, 0.17 mmol).

Postmodification of MCP_{OH}s to Prepare MCPenes

As a typical procedure to synthesize $MCPene_{10}$, a clear solution of DCC (2 g, 11 mmol) in dichloromethane (DCM, 10 mL) was added drop wise into a solution consisting of PA (1.1 mL, 11 mmol), MCP_{OH10} (2.5 g, 3.5 mmol of OH groups), DMAP (0.13 g, 1.1 mmol), and DCM (50 mL) at room temperature under stirring. The resulting mixture was stirred at room temperature for 12 hr. The solids (dicyclohexyl urea) formed as by-products were removed by vacuum filtration and the resulting mixture was concentrated using a rotary evaporator at 30 °C. The resulting mixture was then washed with a saturated aqueous $NaHCO_3$ solution (50 mL) twice and water (50 mL) five times. Residual solids were dried over sodium sulfate and solvents were removed by rotary evaporation. The products were precipitated from hexane and then dried in a vacuum oven at room temperature for 18 hr. Similarly, $MCPene_{30}$ was synthesized with DCC (3.0 g, 15 mmol), PA (1.5 mL, 15 mmol), MCP_{OH30} (1.3 g, 4.9 mmol of OH groups), DMAP (0.18 g, 1.5 mmol), and DCM (60 mL)

Model Kinetic Studies for Photoinduced Thiol-Ene Reactions

MonoSH (40 mg, 0.64 mmol), PA (64 mg, 0.64 mmol), DMPAc (0.17 mL, 30 mg/mL stock solution in $CDCl_3$), and DCM (20 μL) were dissolved in $CDCl_3$ (0.5 mL) in a quartz NMR tube. The resulting mixture was exposed to UV light at λ = 310 nm using a xenon arc lamp (Asahi Spectra, MAX-302) at distance of 17 cm from UV lamp. For other thiols, a similar procedure was applied, except for the use of TriSH (85 mg, 0.21 mmol) and TetraSH (78 mg, 0.16 mmol) in their reactive mixtures.

Photoinduced Thiol-Ene Polyaddition of MCPenes with TetraSH

A series of reactive mixtures consisting of MCPenes, TetraSH, DMPAc, DCM, and $CDCl_3$ was prepared in quartz cuvettes. An aliquot of each mixture (0.6 mL) was taken for ^{1}H-NMR measurements. The rest of the mixture was used for DSC

TABLE 1 Characteristics of MCP_{OH} Random Copolymers Synthesized by ARGET ATRP Initiated with Bz-Br in the Presence of $CuBr_2$/TPMA Complex in Anisole at 60 °C for 4 hrs[a]

MCP_{OH}	HEMA (mol %)	MMA (mol %)	Conv[a]	$M_{n,GPC}$[b] (g/mol)	M_w/M_n[b]	DP[a]/PHEMA	DP[a]/PMMA
MCP_{OH10}	10	90	0.42	7600	1.17	8	44
MCP_{OH30}	30	70	0.24	9800	1.19	26	34

[a] Determined using ^{1}H-NMR.

[b] Determined using GPC calibrated with PMMA standards in DMF as eluent.

measurements. The mole equivalent of vinyl groups was calculated based on the molecular weights of MCPenes determined by ^{1}H-NMR (see Table 1). Typically, to prepare a reactive mixture consisting of $MCPene_{10}$ with TetraSH at $[SH]_0/[vinyl]_0 = 1/1$, the purified $MCPene_{10}$ (0.1 g, 0.12 mmol of vinyl groups), TetraSH (15 mg, 30 μmol), DMPAc (31 μL, 30 mg/mL stock solution in $CDCl_3$), and DCM (20 μL) were dissolved in $CDCl_3$ (3 mL). The resulting mixture in either NMR tube or UV cuvette was exposed to UV light. A reactive mixture consisting of $MCPene_{30}$ with TetraSH at $[SH]_0/[vinyl]_0 = 1/1$ was prepared with the use of the purified $MCPene_{30}$ (0.1 g, 0.29 mmol of vinyl groups), TetraSH (36 mg, 73 μmol), DMPAc (77 μL, 30 mg/mL stock solution in $CDCl_3$), DCM (20 μL), and $CDCl_3$ (3 mL).

Real-Time Rheological Measurements upon UV Irradiation

The viscoelastic properties of reactive mixtures containing MCPenes, TetraSH, DMPAc as a photo initiator, and chloroform (Sigma-Aldrich) were measured at 25 °C using a MCR-301 Rheometer (Anton Paar, Austria) equipped with a UV light lamp (Omnicure series 1000, Lumen Dynamics, Canada) under the small amplitude oscillatory shear (SAOS) mode. Parallel plate fixtures of 8 mm diameter were incorporated for the tests. The lower quartz plate was aligned with the UV lamp in a 15 cm long cylindrical stainless steel tube connected with a quartz wedge. The irradiance of the UV light with wavelength of 320 to 500 nm was found to be 4 mW/cm^2 at the top of the quartz plate. The oscillation frequency was controlled to be 5 Hz with 2% strain.

Experimentally, four reactive mixtures consisting of $MCPene_{10}$ and $MCPene_{30}$ with different amounts of TetraSH were tested. Typically, for the mixture of $MCPene_{10}$ with TetraSH at $[SH]_0/[vinyl\ group]_0 = 1/1$, an aliquot of the dried, purified $MCPene_{10}$ (150 mg), TetraSH (23.4 mg), and DMPAc (2.6 mg) was dissolved in $CHCl_3$ (0.3 mL) to form a clear solution. An aliquot of the solution (0.1 mL) was placed on the plate of the rheometer for measurements.

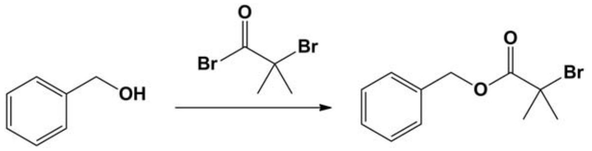
RESULTS AND DISCUSSION

Synthesis of Well-Controlled MCP_{OH}s Having Pendant Hydroxyl Groups Using ATRP

As illustrated in Scheme 3, a benzyl-functionalized ATRP initiator (Bz-Br) was synthesized by the reaction of BA with Br-iBuBr in the presence of Et_3N in THF. After purification by column chromatography, its structure was confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopies (Fig. S1, Supporting Information).

In the presence of the new Bz-Br initiator, a series of ATRP of a mixture of HEMA and MMA mediated with CuBr/TPMA complex in anisole at 60 °C was carried out to synthesize well-defined MCP_{OH}s with narrow molecular weight distributions. An Activator ReGenerated by Electron Transfer (ARGET) process for ATRP (ARGET ATRP) was employed since the ARGET ATRP is a new robust and versatile method utilizing very low amounts of copper metals.[33–35] This method starts with the use of a trace amount of oxidatively-stable Cu(II) species which are reduced to active Cu(I) species in the presence of reducing agents such as $Sn(Oct)_2$. In the experiments, the amounts of HEMA were varied with 10 and 30 mol %, yielding well-defined MCP_{OH}s with different densities of pendant OH groups. The conditions include the initial mole ratio of $[monomers]_0/[Bz\text{-}Br]_0/[CuBr_2/TPMA]_0/[Sn(Oct)_2]_0 = 100/1/0.02/0.2$ and monomers/anisole = 0.33/1 wt/wt. Polymerization was stopped in 4 hrs by exposing reaction mixtures to air. ^{1}H-NMR was used to determine monomer conversion to be 0.42 for MCP_{OH10} with 10 mol % HEMA and 0.24 for MCP_{OH30} with 30 mol % HEMA. The resulting random copolymers were purified by precipitation from hexane three times to remove unreacted monomers, followed by passing them through columns filled with basic aluminum oxides to remove Cu and tin species. Table 1 summarizes the results of MCP_{OH} random copolymers.

The purified, dried copolymers were characterized for molecular weights by GPC and monomer compositions by ^{1}H-NMR. Figure 1 shows GPC traces of the resulting copolymers, suggesting monomodal and narrow molecular weight distribution as $M_w/M_n < 1.2$. Note that asymmetric shape of the GPC traces could be attributed to GPC columns separating



SCHEME 3 Synthesis of a benzyl-functionalized ATRP initiator (Bz-Br).

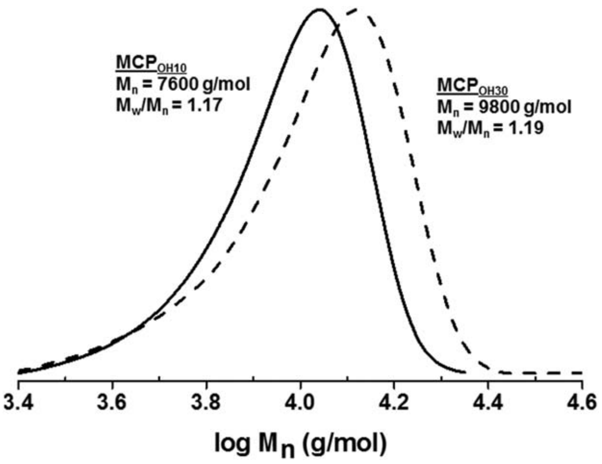


FIGURE 1 GPC traces of MCP_{OH10} and MCP_{OH30}.

polymeric species. Their molecular weights were determined to be the number average molecular weight, $M_n = 7600$ g/mol for MCP_{OH10} and $M_n = 9800$ g/mol for MCP_{OH30}. As an example, Figure 2(a) shows the typical ^{1}H-NMR spectrum of the purified MCP_{OH10}. A characteristic peak for the initiating species appeared as a multiplet at 7.3 ppm corresponding to five phenyl protons (a). For PHEMA units, two doublets at 4.2 ppm (f) and 3.8 ppm (g) correspond to two methylene protons adjacent to pendant ester groups and hydroxyl group, respectively. For PMMA units, a singlet at 3.6 ppm (e) corresponds to three methoxy protons. The integral ratios of these peaks were used to determine the number of PHEMA units by [(f/2)/(a/5)] and PMMA units by [(e/3)/(a/5)]. These unit numbers are denoted as the DP (degree of polymerization) in Table 1. The DP was 8 for PHEMA and 44 for PMMA for MCP_{OH10}, but 26 for PHEMA and 34 for PMMA for MCP_{OH30}. These results suggest the successful synthesis of MCP_{OH} copolymers with differing densities of pendant OH groups. Interestingly, the content of PHEMA incorporated into the copolymers can be calculated to be 15 mol % for MCP_{OH10} and 45 mol % for MCP_{OH30}; these values are larger than 10 and 30 mol % in feed, respectively.

Synthesis of MCPenes by Postmodification of MCPOHs with PA

Well-controlled MCP_{OH} copolymers having pendant OH groups reacted with PA using the carbodiimide coupling reaction in the presence of DCC in anhydrous THF, yielding well-defined methacrylate copolymer polyenes (MCPenes). Figure 2(b) shows the example of ^{1}H-NMR spectrum of $MCPene_{10}$. A new peak at 4.4 ppm (g′), corresponding to new methylene protons adjacent to the ester groups of PA moieties, as well as other new peaks (h, i, j, k) appeared. Furthermore, the peak at 3.8 ppm (g) corresponding to methylene protons adjacent to OH groups completely disappeared. These results suggest quantitative esterification of pendant OH groups with PA molecules (≈100% conversion) to successfully synthesize well-controlled $MCPene_{10}$. Similar results were obtained for $MCPene_{30}$.

Model Studies of Photoinduced Thiol-Ene Reactions

To get a better insight into kinetics of photoinduced thiol-ene addition of MCPenes having pendant vinyl ($CH_2{=}CH{-}$) groups, model studies were conducted with PA, a precursor for MCPenes. Three reactive mixtures were prepared by mixing aliquots of PA with various thiols having different numbers of SH groups including Mono, Tri, and TetraSH under the initial mole equivalent ratio of $[SH]_0/[\text{vinyl group}]_0 = 1/1$ [Fig. 3(a)].

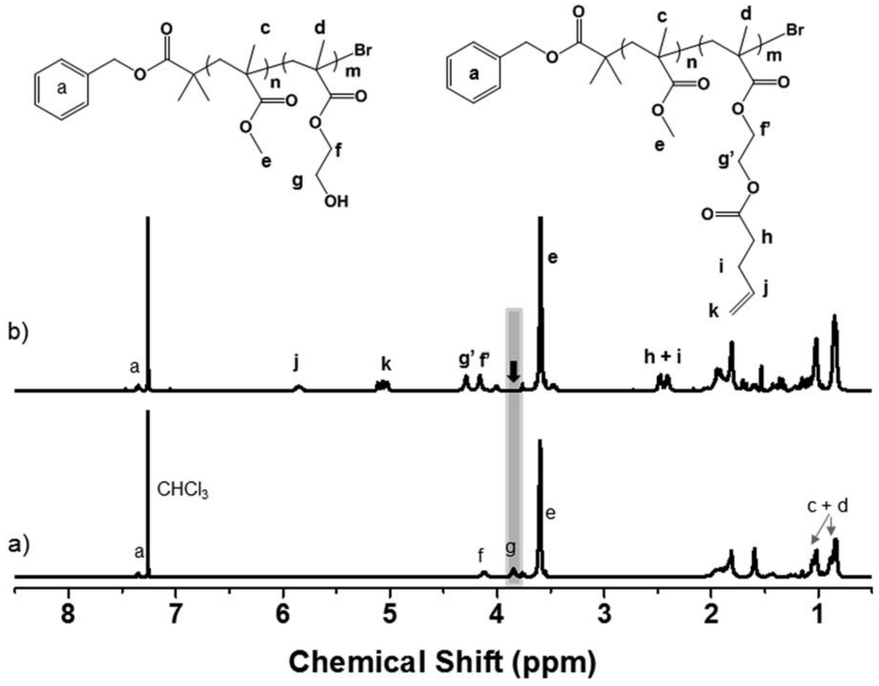


FIGURE 2 ^{1}H-NMR spectra of MCP_{OH10} (a) and $MCPene_{10}$ (b) in $CDCl_3$.

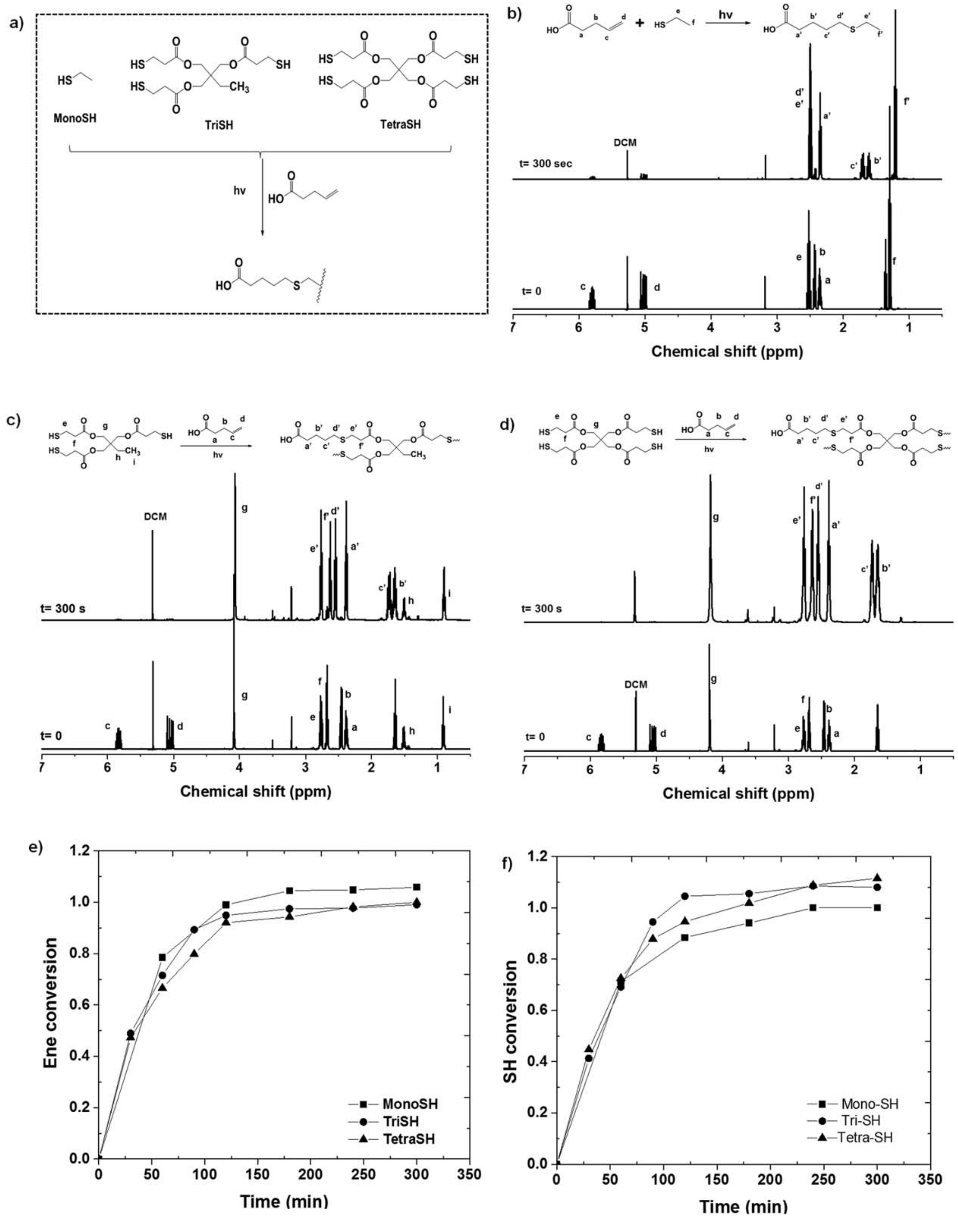


FIGURE 3 Scheme of photoinduced thiol-ene addition of PA with various thiols having different SH groups (a), ^{1}H-NMR spectra of their mixtures before ($t = 0$) and after 300 s of UV irradiation in the presence of DMPAc in $CDCl_3$ (b–d), and conversion of ene (e) and SH (f) over UV irradiation time.

Figure 3(b,d) shows overlaid ^{1}H-NMR spectra of the three mixtures before ($t = 0$) and after 300 s of UV irradiation at $\lambda = 310$ nm in the presence of DMPAc in a quartz NMR tube in $CDCl_3$. For all three mixtures, the consumption of vinyl groups of PA molecules can be followed with the disappearance of a peak at 5.8 ppm (c) corresponding to a vinyl

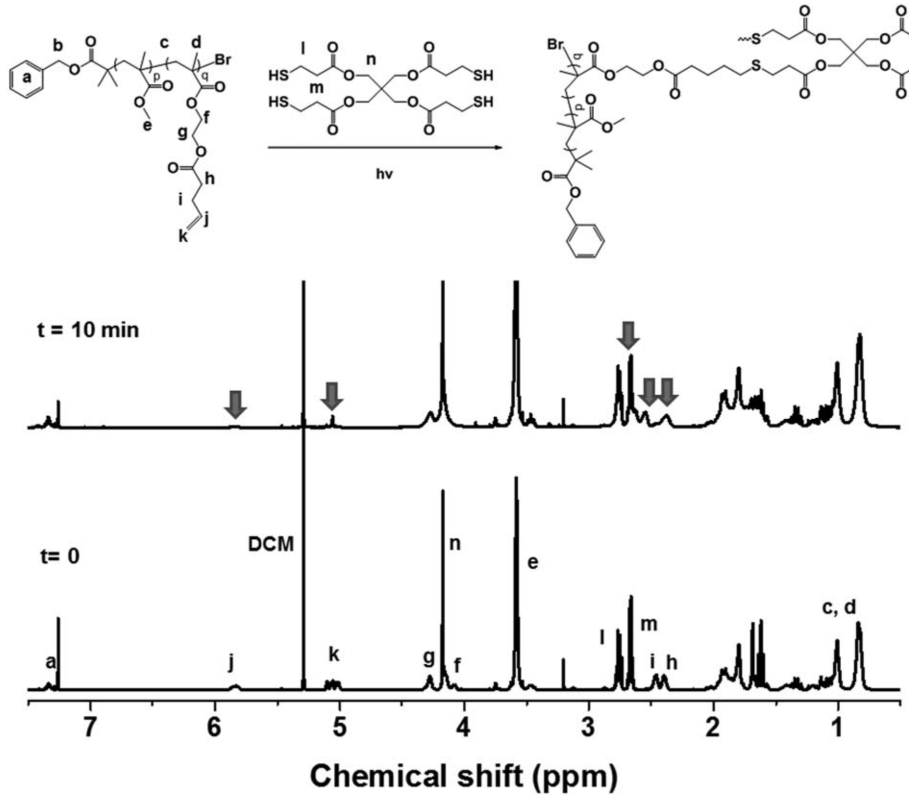


FIGURE 4 ^{1}H-NMR spectra of the mixtures consisting of MCPene$_{10}$ with TetraSH at $[SH]_0/[vinyl]_0 = 1/1$ before and after 10 min of UV irradiation in the presence of DMPAc in $CDCl_3$.

proton and a concomitant appearance of a new peak at 1.7 ppm (c′). The integral ratio of the vinyl proton $[(c'/2)/(c + (c'/2))]$ allows for the calculation of the conversion of vinyl groups (i.e. ene conv). The consumption of SH groups of three different thiols is somewhat complicated. For MonoSH, a shift of a multiplet at 1.3 ppm (f) corresponding to its methyl protons to the new multiplet appearing at 1.2 ppm (f′) can be monitored as a consequence of the formation of new sulfide bonds through thiol-ene addition. The integral ratio of the peaks $[f'/(f + f')]$ can be used to calculate the conversion of thiols to the corresponding sulfides through thiol-ene addition (i.e. SH conv). For TriSH and TetraSH, a shift of a peak at 2.7 ppm (f) corresponding to their methylene protons adjacent to carbonyl groups to the new peak appearing at 2.45 ppm (f′) can be monitored. Since the peak at 4.2 ppm corresponding to methylene protons (g) remained unchanged during the reactions, the integral ratio of the peaks $[f'/g]$ allows for the calculation of the SH conv.

Figure 3(e,f) shows the kinetics of ene and SH conversions. For the three mixtures consisting of different thiols, conversions were fast, reaching >90% within 100 s of UV irradiation. Within experimental errors, the rates of ene and SH conversions are similar for the three mixtures, suggesting that thiol-ene addition through the formation of sulfide bonds is the dominant mechanism in the formation of crosslinked films for vinyl-type enes. The consumption of vinyl groups can be attributed to two competing reactions: thiol-ene radical addition and free radical polymerization (FRP) of ene initiated upon photolysis. These competing thiol-ene radical addition and FRP depends on the structures of enes. For acrylates, both reactions are competitive, while thiol-ene radical polyaddition is dominant for olefins, norbornenes, and vinyl ethers.[6,36–38] Our results are consistent with these reported results. In addition, the conversions of ene and SH were similar for the three reactive mixtures, suggesting no significant effects of the number of SH groups on the rate of thiol-ene radical addition.

Formation of Photoinduced Thiol-Ene Crosslinked Networks Based on MCPenes

Given the results obtained from the model studies, photoinduced thiol-ene polyaddition of the resulting linear MCPenes with TetraSH as a model polythiol was examined. First, aliquots of the purified, dried MCPene$_{10}$ were mixed with different amounts of TetraSH in the presence of DMPAc in a quartz NMR tube. The initial mole equivalent ratios of functional groups were varied to be $[SH]_0/[vinyl]_0 = 0.5/1$, 1/1, and 2/1. Interestingly, our preliminary results suggest that longer irradiation time is required for complete conversion. As an example, Figure 4 shows ^{1}H-NMR spectra of the reactive mixture at $[SH]_0/[vinyl]_0 = 1/1$ before and after 10 min of UV irradiation. Similar to the model kinetic studies above, the typical peaks (j, k) corresponding to vinyl protons of PA moieties disappeared. Note that a trace of peak at 5.1 ppm corresponds to photoinitiating moieties. The typical peaks (l, m)

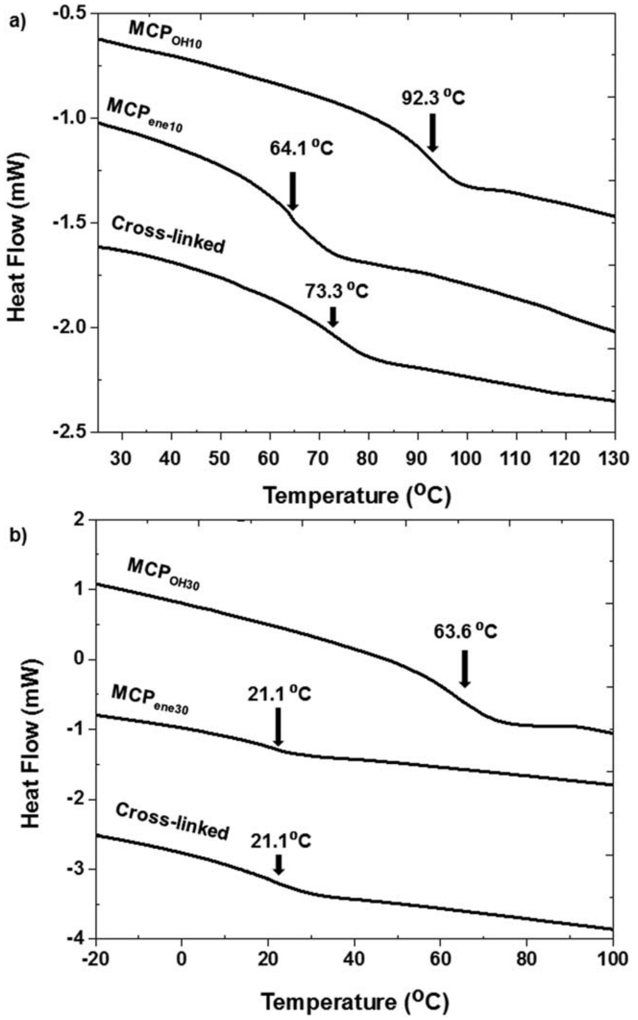


FIGURE 5 DSC traces of P(MMA-*co*-HEMA) designed with 10 mol% (a) and 30 mol% HEMA (b) before (MCP_{OH}) and after (MCPene) functionalization with PA, as well as photoinduced crosslinked films of MCPene with TetraSH. DSC traces are shifted vertically in order to superimpose them in the same graph.

for TetraSH were shifted. These results suggest the complete consumption of both vinyl and SH groups to form crosslinked network through the formation of sulfide bonds by thiol-ene radical polyaddition. For other reactive mixtures with different mole equivalent ratios of $[SH]_0/[vinyl]_0$ to be 0.5/1 and 2/1, complete consumption of both vinyl and SH groups was observed within 10 min of UV irradiation (Fig. S2, Supporting Information). Similar results were observed for the reactive mixture consisting of $MCPene_{30}$ with TetraSH at $[SH]_0/[vinyl]_0 = 1/1$ (Fig. S3, Supporting Information).

Thermal Analysis for Thiol-Ene Crosslinked Films

DSC was used to measure thermal properties including glass transition temperature (T_g) of MCP_{OH}s and MCPenes before and after the occurrence of crosslinking reactions. As seen in Figure 5, only one T_g value appeared at 92.3 °C for MCP_{OH10} and at 64.1 °C for MCP_{OH30}, suggesting the decrease in T_g of MCP_{OH} copolymers with an increasing amount of PHEMA units. Using Fox equation with the reported T_g of 100 °C for PMMA homopolymer (atactic) and 57 °C for PHEMA homopolymer, the predicted T_g values were estimated to be 99 °C for MCP_{OH10} containing 18 wt % HEMA units and 79 °C for MCP_{OH30} containing 50 wt % HEMA units. Although the measured and predicted values are slightly different, the exhibition of one glass transition suggests that MCPenes are random copolymers consisting of HEMA and MMA units. After the modification of pendant OH groups with PA, the T_g values of MCPenes decreased from 99 to 64 °C for $MCPene_{10}$ and from 79 to 21 °C for $MCPene_{30}$. Such decrease in T_g values is attributed to the increase in bulkiness of the side chains. After the occurrence of crosslinking with TetraSH, the T_g value slightly increased from 64 to 73 °C for $MCPene_{10}$, while it remained unchanged to be 21 °C for $MCPene_{30}$. It is not clear, but the plausible reason for T_g value of MCPene30 being unchanged after crosslinking is due to the balance of an increasing crosslinking density, increasing T_g, and an increasing pendant bulkiness, decreasing T_g.

Real-Time Viscoelastic Properties upon UV Irradiation

Furthermore, viscoelastic and mechanical properties were assessed for the photo-induced thiol-ene crosslinked networks prepared from the reactive mixtures consisting of MCPenes and TetraSH. The important parameters that significantly influence the course of photo-induced thiol-ene crosslinking were examined upon UV irradiation. First, the amount of TetraSH defined as the initial mole equivalent ratio of $[SH]_0/[vinyl]_0$ with $MCPene_{10}$ was examined. Figure 6(a) shows the evolution of elastic modulus (G') over measuring time for three reactive mixtures with different initial mole equivalent ratios of $[SH]_0/[vinyl]_0 = 0.5/1$, 1/1, and 2/1. For all three samples, the G' values abruptly increased at the onset of UV irradiation ultimately reaching a plateau (maximum G' values). However, to reach this plateau, it took >40 s for a 0.5/1 mixture and >25 s for the 1/1 mixture, while it took <10 s for the 2/1 mixtures. As can be obtained from the comparison in Figure 7, when the amount of TetraSH increased in the mixtures, the difference of G' values at the onset of irradiation and the plateau ($\Delta G'$) also increased. Interestingly, the $\Delta G'$ value for the 2/1 mixture is slightly smaller than that for the 1/1 mixture. The plausible reason is the formation of dangling chains of SH groups from the network which can be attributed to excess TetraSH in the 2/1 mixture. Figure 6(b) shows tan δ curves which represent the ratio of viscous modulus to elastic modulus (G''/G'). Similarly, the tan δ decreased with an increasing amount of TetraSH due to the more dominant effect of elastic modulus. These results suggest that the rate and extent of photoinduced thiol-ene crosslinking of MCPenes with TetraSH increased with an increasing amount of TetraSH in the reactive mixtures.

Next, the amount of vinyl groups of MCPenes with $MCPene_{10}$ versus $MCPene_{30}$ in the reactive mixtures of $[SH]_0/[vinyl]_0 = 1/1$ was examined. Figure 6(c,d) shows the evolution of G' and tan δ over the measuring time. With an increase in the amount of vinyl groups in MCPenes (e.g. from $MCPene_{10}$

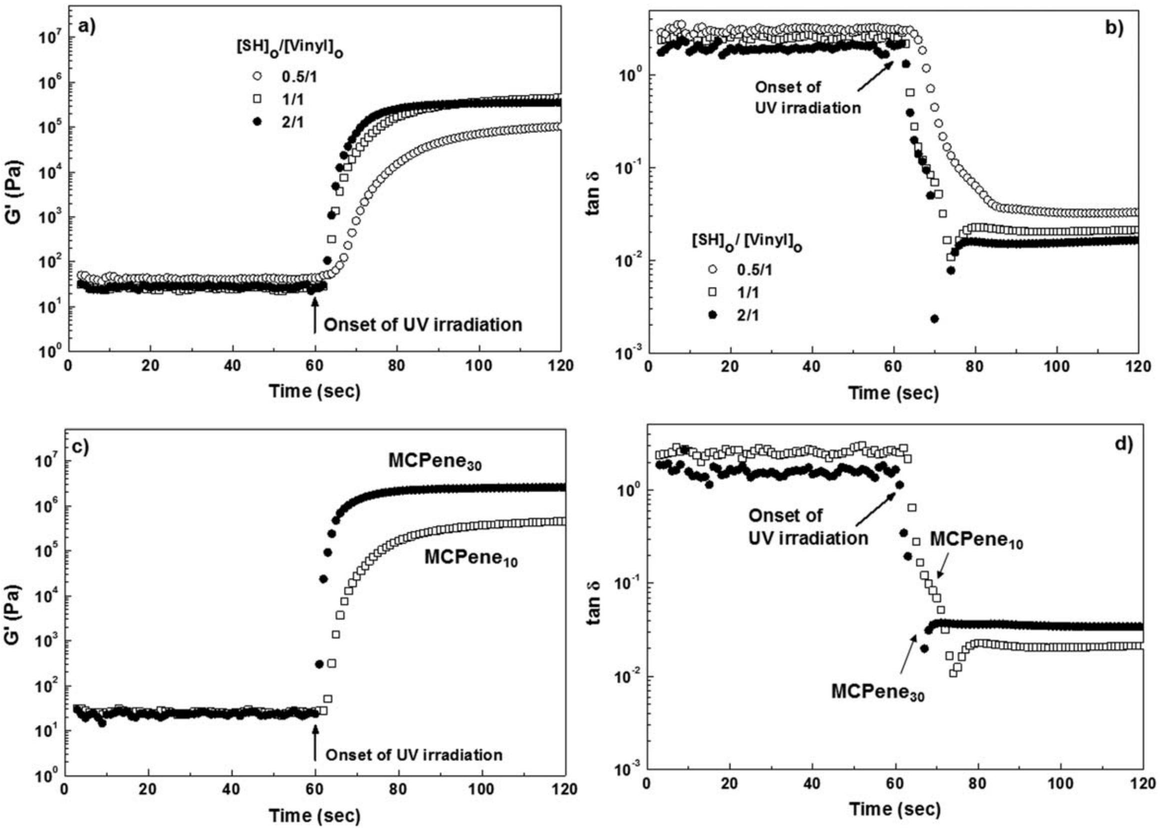


FIGURE 6 Evolution of elastic modulus (a, c) and tan δ (b, d) over UV irradiation time for reactive mixtures consisting of MCPene$_{10}$ with different amounts of TetraSH defined as initial mole equivalent ratios of $[SH]_0/[vinyl]_0 = 0.5/1$, 1/1, and 2/1 (a, b) and reactive mixtures consisting of MCPene$_{10}$ and MCPene$_{30}$ with TetraSH at $[SH]_0/[vinyl]_0 = 1/1$ (c, d).

to MCPene$_{30}$), the elastic modulus considerably increased at the onset of UV irradiation. Figure 7 also shows larger ($\Delta G'$) value for the MCPene$_{30}$ mixture, compared with MCPene$_{10}$ mixture. The final tan δ value of the MCPene$_{30}$ mixture was also higher than that of MCPene$_{10}$, presumably due to the higher viscous nature of a mixture containing MCPene$_{30}$.

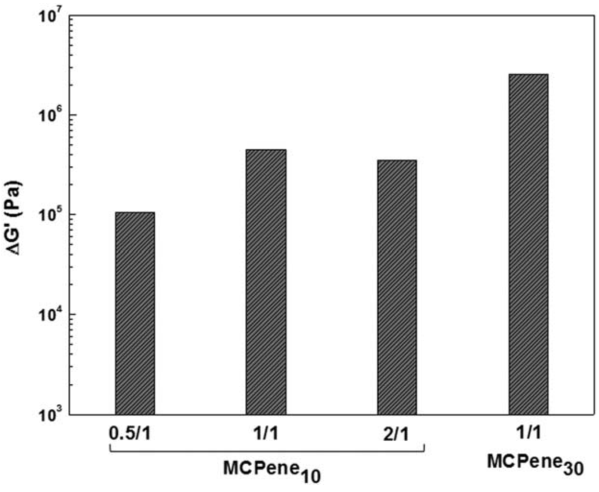


FIGURE 7 $\Delta G'$ modulus at onset and 20 s UV irradiation in the oscillation shear mode under UV irradiation for reactive mixtures consisting of MCPenes and TetraSH in chloroform with different mole equivalent ratios of $[SH]_0/[vinyl]_0$.

CONCLUSIONS

Multifunctional MCPenes having pendant vinyl groups were prepared by a combination of ATRP and facile carbodiimide coupling reaction. ARGET ATRP of monomer mixtures consisting of different amounts of HEMA and MMA proceeded in a living manner to yield well-defined MCP$_{OH}$s with different densities of pendant OH groups and narrow molecular weight distribution ($M_w/M_n < 1.2$). The following postmodification of OH groups with carboxylic acid groups of PA resulted in MCPenes with different densities of pendant vinyl groups. With the selection of PA as a precursor of MCPenes, kinetic studies of UV-induced thiol-ene addition of various thiols (MonoSH, TriSH, and TetraSH) suggest no significant effect of the number of SH groups on the addition rate with vinyl groups. In addition, the consumption rate of ene and SH groups was similar for the reactive mixtures. These results suggest that the consumption of vinyl groups is attributed predominantly to thiol-ene radical addition to form the new sulfide bonds, with negligible competition with FRP of enes initiated by photolysis. Consequently, MCPenes reacted with TetraSH to yield mechanically coherent, crosslinked films through the formation of sulfide bonds between pendent vinyl groups and SH groups, confirmed by ^{1}H-NMR and DSC results. Furthermore, viscoelastic results suggest that elastic modulus as a measure of mechanical properties increased with an increasing amount of SH groups and vinyl groups in the reactive mixtures. These results suggest that UV-induced crosslinked films consisting of MCPenes with TetraSH exhibit rapid cure, uniform network, and enhanced and tunable mechanical properties; these properties are required for high performance coating materials.

For the perspectives to be useful as surface coating materials, MCPenes having pendant vinyl groups can be mixed with MCPshS having pendant SH groups. Photoinduced thiol-ene addition of the mixtures will enable the formation of sulfide-crosslinked films based on pure MCPs. With the selection of monomer compositions of MCPenes and MCPshS (i.e. high and low T_g as well as hydrophilicity and hydrophobicity), the film properties such as mechanical properties with crosslinking densities and phase separation based on miscibility of the resulting thiol-ene films can be modulated for end-user coating applications.

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