Macromolecules

Article

pubs.acs.org/Macromolecules

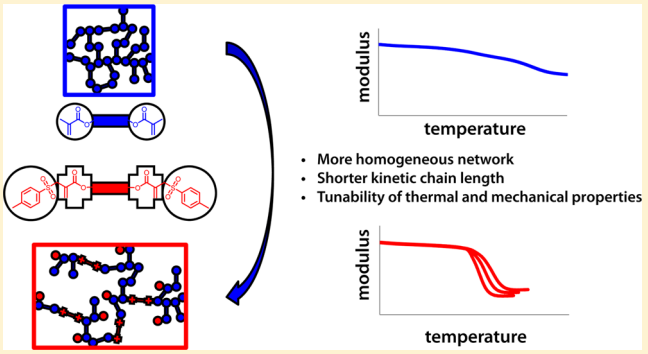
β-Allyl Sulfones as Addition−Fragmentation Chain Transfer Reagents: A Tool for Adjusting Thermal and Mechanical Properties of Dimethacrylate Networks

Christian Gorsche,[†,‡] Markus Griesser,[†,‡] Georg Gescheidt,[§] Norbert Moszner,[‡,∥] and Robert Liska*[,†,‡]

[†]Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163 MC, 1060 Vienna, Austria
[‡]Christian-Doppler-Laboratory for Photopolymers in Digital and Restorative Dentistry, Getreidemarkt 9, 1060 Vienna, Austria
[§]Institute of Physical and Theoretical Chemistry, NAWI Graz, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria
[∥]Ivoclar Vivadent AG, 9494 Schaan, Liechtenstein

Supporting Information

ABSTRACT: Dimethacrylates are known to have good photoreactivity, but their radical polymerization usually leads to irregular, highly cross-linked, and brittle polymer networks with broad thermal polymer phase transitions. Here, the synthesis of mono- and difunctional β-allyl sulfones is described, and those substances are introduced as potent addition−fragmentation chain transfer (AFCT) reagents leading to dimethacrylate networks with tunable properties. By controlling the content and functionality of said AFCT reagents, it is possible to achieve more homogeneous networks with a narrow glass transition and an adjustable glass transition temperature (T_g), rubber modulus of elasticity (E_r), and network density. In contrast to dimethacrylate networks containing monomethacrylates as reactive diluents, the network architecture of the β-allyl sulfone-based dimethacrylate networks is more homogeneous and the tunability of thermal and mechanical properties is much more enhanced. The reactivity and polymerization were investigated using laser flash photolysis, photo-DSC, and NMR, while DMTA and swellability tests were performed to characterize the polymer.



INTRODUCTION

UV-photopolymerization of (meth)acrylates paves the way to convenient and low-energy processability.[1,2] Polymers derived via photopolymerization are attractive for protective and decorative coatings,[3,4] biomedical research,[5−8] and 3D-lithography techniques.[9−13] While enabling a number of favorable properties such as rapid curing, low-energy processing, good storage stability, and the absence of solvents, the attainable material properties are limited. This is strongly due to the lack of control over the radical polymerization. Conventional UV-photopolymerization of cross-linking monomers can be described as a radical chain growth polymerization, leading to materials with uncontrolled and inhomogeneous network architecture. As a result, this network architecture yields materials with broad thermal phase transitions and brittle networks. Nevertheless, some photopolymerized resins containing a substantial amount of reactive diluent (monofunctional monomer) and cross-linkers with flexible spacers (e.g., ethylene glycol-based) may form materials having a narrow T_g and enable tunability of mechanical properties.[14] However, such materials may generate toxicity problems due to the migration of unreacted monofunctional monomers. Also, the formed networks remain inhomogeneous due to the uncontrolled radical chain growth mechanism.

For the synthesis of photopolymer networks with increased homogeneity, a controlled radical polymerization is desirable. Alternatively, a change from the radical chain growth mechanism toward a step growth-like system is a possibility. A number of methods for controlled free radical polymerization have been described in the literature (e.g., reversible addition−fragmentation chain transfer (RAFT)[15] and atom-transfer radical polymerization (ATRP)[16]). AFCT[15] reagents also have the potential to regulate radical polymerization reactions. The AFCT chemistry proceeds similarly to the polyreaction of thiol−ene/yne[17−19] systems in a mixed chain growth/step growth-like mechanism without having their drawbacks of poor storage stability and bad odor. For photopolymerizable cross-linking systems the AFCT approach seems to be the most promising technique, since RAFT and ATRP systems tend to show strong absorbance in the UV/vis light region.

Received: July 29, 2014
Revised: October 3, 2014

   dx.doi.org/10.1021/ma501550b | *Macromolecules* XXXX, XXX, XXX−XXX

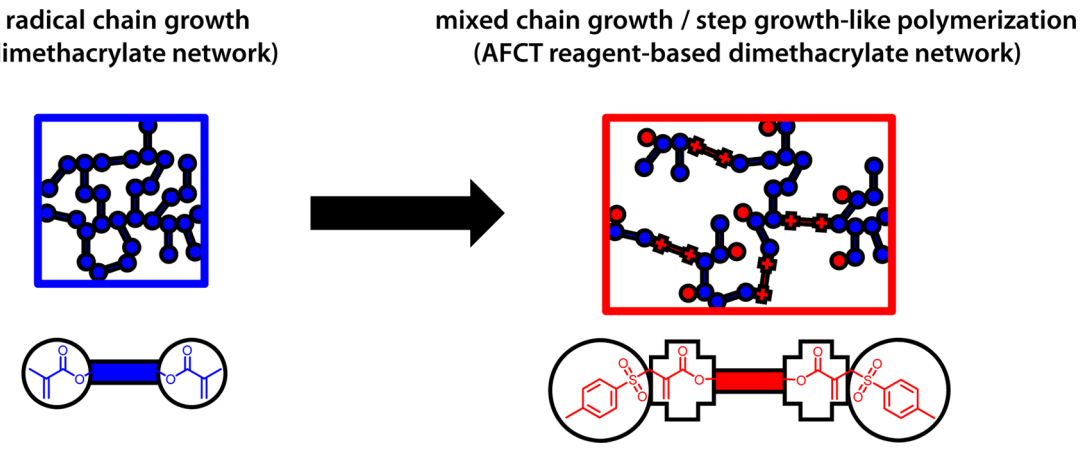


Figure 1. Simplified models of network architectures.

The AFCT mechanism shows great potential in pushing an uncontrolled radical chain growth polymerization reaction toward a step growth-like manner (Figure 1).[15,16] By adding AFCT reagents to a radical polymerizable cross-linking monomer mixture, the uncontrolled radical chain growth mechanism can be altered and would ultimately produce materials with a more homogeneous network structure and, consequently, improved mechanical properties. β-Allyl sulfones are promising AFCT reagents, and basic polymerization studies on such substances have already been performed.[20,21] However, hardly any AFCT reagents aside from β-allyl sulfides[22] have been mentioned for the synthesis of photopolymerized cross-linked functional materials. Research on AFCT reagents thus far was mainly focused on molecular weight control of linear polymers (e.g., styrene[20] and methyl methacrylate[23]), for the synthesis of hyperbranched polymers[24] or end-group functionalization.[20,25,26] In general, highly cross-linked polymers with AFCT reagents potentially pave the way for applications such as shape memory polymers[14,27] and covalent adaptable networks.[28]

In this work we show, how β-allyl sulfones (AFCT reagents) regulate the architecture of photopolymerized dimethacrylate networks and consequently generate more homogeneous polymer networks. By optimizing the synthesis of β-allyl sulfones,[29] a mono- and difunctional AFCT reagent have successfully been isolated. The reactivity and the general mechanism of β-allyl sulfones in photopolymerizations were investigated by means of laser flash photolysis and photo-DSC. β-Allyl sulfone-based dimethacrylate networks have been formed through photopolymerization and were compared to a standard dimethacrylate network and dimethacrylate networks containing a reactive monomethacrylate diluent. The tunability of properties such as polymerization time (determined via photo-DSC), T_g, E_r (determined via DMTA), network density, and swellability has been evaluated.

EXPERIMENTAL SECTION

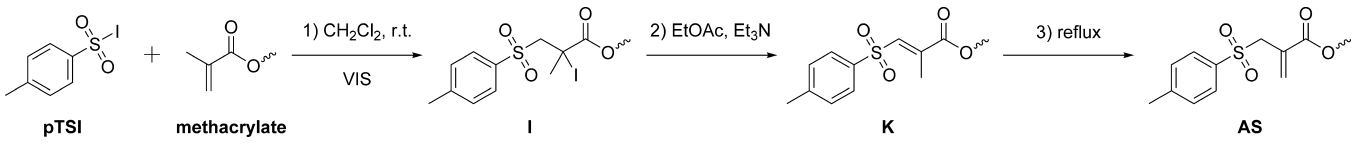
Materials and General Methods. The photoinitiator (PI) bis(4-methoxybenzoyl)diethylgermanium (Ivocerin) and the monomers 1,10-decanediol dimethacrylate (D3MA) and urethane dimethacrylate (UDMA, isomeric mixture; CAS: 72869-86-4) were provided by Ivoclar Vivadent AG. Tetra(ethylene glycol) dimethacrylate (TTEGDMA) was purchased from UCB Chemicals. Di(ethylene glycol) ethyl ether methacrylate (DEGEMA) and methyl methacrylate (MMA) were purchased from Sigma-Aldrich. Bis(2,6-dimethoxybenzoyl)(2,4,4-trimethylpentyl)phosphine oxide (CGI403) was provided by Ciba SC. NMR spectra were recorded on a Bruker AC 200 at 200 MHz (50 MHz for ^{13}C); chemical shifts are given in ppm and were referenced to the solvent residual peak ($CDCl_3$). Multiplicities are referred to as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants are given in Hz. Silica gel chromatography was performed with a Büchi MPLC-system equipped with the control unit C-620, fraction collector C-660, and UV-photometer C-635. Commercial grade reagents and solvents were used without further purification.

Synthesis of *p*-Toluenesulfonyl Iodide (pTSI). All work steps were performed under light protection by working in the yellow light lab where wavelengths below 480 nm are filtered (adhesive foils of the company IFOHA were used to cover windows and fluorescent lamps). At first, iodine (9.14 g, 36 mmol) was dissolved in approximately 150 mL of ethanol and then added to a stirred solution of sodium *p*-toluenesulfinate (6.41 g, 36 mmol, 0.1 M in water). After the addition was completed, the reaction was stirred for another 15−30 min. Then the yellow precipitate (pTSI) was filtered by suction filtration and washed with water. Afterward, the precipitate was dissolved in a minimal amount of toluene and dried over Na_2SO_4. The solution was then filtered into the same amount of cold petrol ether and pTSI was crystallized at −20 °C. The yellow solid was filtered, washed with cold petrol ether, and dried under vacuum. pTSI was isolated in 60% yield (6.09 g). ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 7.75 (d, ^3J = 8.2 Hz, 2H; Ar−H), 7.34 (d, ^3J = 8.2 Hz, 2H; Ar−H), 2.48 (s, 3H; Ar−CH_3). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 147.5 (C4), 146.3 (C4), 129.7 (C3), 125.4 (C3), 21.8 (C1). Analytical data were in accordance with literature values.[30]

Synthesis of β-Allyl Sulfones. The first step of this synthesis was prepared under light protection. Depending on the target compound 1 equiv (1.69 g, 6 mmol; for monofunctional β-allyl sulfone MAS) or 2 equiv (3.38 g, 12 mmol; for difunctional β-allyl sulfone DAS) of pTSI was placed into separate 100 mL round-bottom flasks, and 50 mL of CH_2Cl_2 was added to each. Then 1 equiv of DEGEMA (1.21 g; for MAS) or 1 equiv of TTEGDMA (1.98 g; for DAS) was added to the reaction solutions. At this point the reaction solutions were placed in the light (regular light bulb), and both reactions were stirred until the methacrylate double bonds disappeared in the ^{1}H NMR spectra (additional TLC monitoring). In both cases the reaction took approximately 3 h. After completion of the reaction step, 50 mL of ethyl acetate was added to the reaction solutions, and all following steps were again performed under light protection. CH_2Cl_2 was evaporated, and the ethyl acetate phase washed with a 5 wt % solution of sodium dithionite (2 × 30 mL) and water (2 × 30 mL). The collected aqueous phases were reextracted with 30 mL of ethyl acetate, and the combined organic phases were dried over Na_2SO_4. The solutions were filtered and placed into three-neck round-bottom flasks with reflux condensers. The reactions were flushed with argon, and 5 equiv of freshly distilled triethylamine (3.04 g, 30 mmol) was added slowly to both reactions. The reactions were refluxed, and the progress

dx.doi.org/10.1021/ma501550b | *Macromolecules* XXXX, XXX, XXX−XXX

Scheme 1. Synthesis of β-Allyl Sulfones (AS)



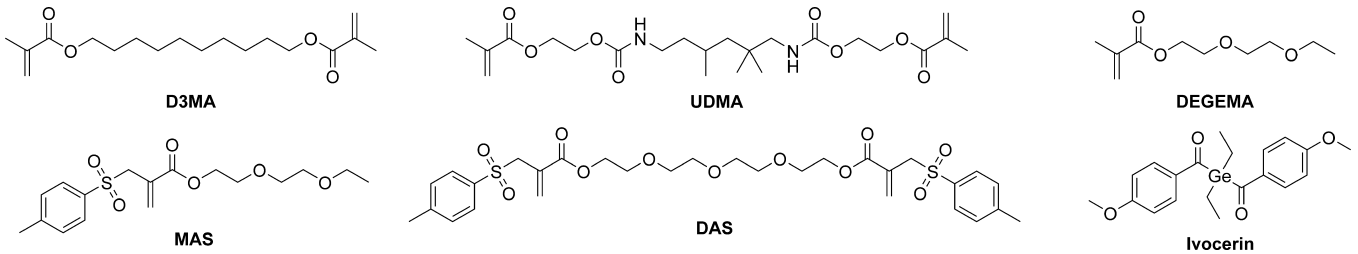


Figure 2. Monomers, AFCT reagents, and PI used for network studies: 1,10-decanediol dimethacrylate (D3MA), urethane dimethacrylate (UDMA), di(ethylene glycol) ethyl ether methacrylate (DEGEMA), mono-β-allyl sulfone (MAS), di-β-allyl sulfone (DAS), and bis(4-methoxybenzoyl)-diethylgermanium (Ivocerin).

of the reactions was tracked via ^{1}H NMR analysis. After completion of the reactions, the solutions were cooled and then washed with 1 N HCl (2 × 50 mL) and water (50 mL). The aqueous phases were reextracted with ethyl acetate and the combined organic phases dried over Na_2SO_4. The solvent was evaporated, and the crude products were purified via silica column chromatography (PE/EE: 1/3).

2-(2-Ethoxyethoxy)ethyl 2-(tosylmethyl)acrylate (MAS): 56% yield (1.20 g); ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 7.73 (d, ^3J = 8.2 Hz, 2H; Ar−H), 7.32 (d, ^3J = 8.2 Hz, 2H; Ar−H), 6.52 (s, 1H; =CH_2), 5.89 (s, 1H; =CH_2), 4.12 (m, 4H; SO_2−CH_2−, OOC−CH_2−), 3.62 (m, 6H; −CH_2−O−CH_2−CH_2−), 3.53 (q, ^3J = 7.0 Hz, 2H; O−CH_2−CH_3), 2.43 (s, 3H; Ar−CH_3), 1.21 (t, ^3J = 7.0 Hz, 3H; O−CH_2−CH_3); ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm): 164.8 (C═O), 144.9 (C4), 135.4 (C4), 133.6 (C2), 129.7 (C3), 128.9 (C4), 128.8 (C3), 70.7 (C2), 69.8 (C2), 68.8 (C2), 66.7 (C2), 64.5 (C2), 57.5 (C2), 21.6 (C1), 15.1 (C1); Anal. Calcd for $C_{17}H_{24}O_6S$: C 57.28, H 6.79, S 9.00. Found: C 56.51, H 6.71, S 8.72.

((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl) bis(2-(tosylmethyl)acrylate) (DAS): 70% yield (2.68 g); ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 7.73 (d, ^3J = 8.2 Hz, 4H; Ar−H), 7.32 (d, ^3J = 8.2 Hz, 4H; Ar−H), 6.52 (s, 2H; =CH_2), 5.89 (s, 2H; =CH_2), 4.14 (m, 8H; OOC−CH_2−, SO_2−CH_2−), 3.62 (m, 12H; −CH_2−O−CH_2−CH_2−), 2.43 (s, 6H; Ar−CH_3); ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm): 164.9 (C═O), 144.9 (C4), 135.4 (C4), 133.6 (C2), 129.7 (C3), 128.9 (C4), 128.8 (C3), 70.7 (C2), 68.8 (C2), 64.5 (C2), 57.5 (C2), 21.6 (C1); Anal. Calcd for $C_{30}H_{38}O_{11}S_2$: C 56.41, H 6.00, S 10.04. Found: C 56.36, H 5.89, S 9.84.

Synthesis of Polymer Networks for Testing. All prepared monomer formulations were mixed with 0.97 mol % PI (Ivocerin) in an ultrasonic bath for 30 min at ambient temperature. The formulations with β-allyl sulfones added showed good storage stability over the course of 90 days. Rheological data have been provided in the Supporting Information (Table S1). For photo-DSC measurements, the monomer formulations were used. For DMTA analysis and swellability experiments, polymer specimens were fabricated by pouring the monomer formulations into a silicone mold (sticks, 5 × 2 × 40 mm^3 for DMTA; disks, d = 4 mm, h = 2 mm for swellability tests) and then curing the samples for 20 min in a Lumamat 100 light oven (provided by Ivoclar Vivadent AG) with six Osram Dulux L Blue 18 W lamps. The emitted wavelength spectrum was 400−580 nm at a measured total intensity of ∼20 mW cm^{-2} determined with an Ocean Optics USB 200+ spectrometer.

Laser Flash Photolysis. Nanosecond transient absorption experiments were performed on a LKS80 spectrometer (Applied Photophysics, UK). Excitation was performed using the third harmonic (355 nm, 10−20 mJ/pulse, ca. 8 ns) of a Spitlight Compact 100 (InnoLas, Germany) Nd:YAG laser. Concentration of CGI403 in acetonitrile was adjusted to achieve an absorbance of ca. 0.3 at 355 nm. The transient absorption spectra were recorded in a quartz cuvette (1 cm × 1 cm). Samples were purged and constantly bubbled with argon to refresh the sample and avoid sample decomposition. The rate constants for the addition of the phosphinoyl radicals to the monomer double bonds, k_{add}, were determined in pseudo-first-order according to the equation $k_{obs} = k_0 + k_{add}c_{quencher}$. Furthermore, the global analysis software Pro-K (Applied Photophysics) was employed.

Photo-DSC. A Netzsch DSC 204 F1 with autosampler was used to perform the photo-DSC measurements. All measurements were conducted isocratic at 25 °C under a N_2 atmosphere. 10 ± 1 mg of a monomer formulation was weighed in accurately into an aluminum DSC pan, which was then placed in the DSC chamber. After the sample chamber had been purged with N_2 (N_2 flow = 20 mL min^{-1}) for 4 min, the samples were irradiated with filtered UV-light (400−500 nm) from an Exfo OmniCure series 2000 for a defined duration at an intensity of 1 W cm^{-2} at the exit of the light guide (corresponds to ∼20 mW cm^{-2} on the surface of the sample). The heat flow of the polymerization reaction was recorded as a function of time.

Dynamic Mechanical Thermal Analysis (DMTA). DMTA measurements were performed with an Anton Paar MCR 301 with a CTD 450 oven and a SRF 12 measuring system. Polymer specimens (∼5 × 2 × 40 mm^3) were tested in torsion mode with a frequency of 1 Hz and strain of 0.1%. The temperature was increased from −100 to 200 °C with a heating rate of 2 °C min^{-1}. The storage modulus and the loss factor of the polymer samples were recorded with the software Rheoplus/32 V3.40 from Anton Paar.

Swellability Tests. The polymer disks (3 disks per sample) were submerged in ethanol and stored at ambient temperature for 7 days. 200 ppm of hydroquinone monomethyl ether was added to the ethanol to prevent free-radical reactions. The ethanol was replaced two times, after 1 and 4 days. The polymer disks were dried using a paper towel and then weighed. Afterward, the disks were placed in a 60 °C vacuum oven and dried until a constant weight was reached.

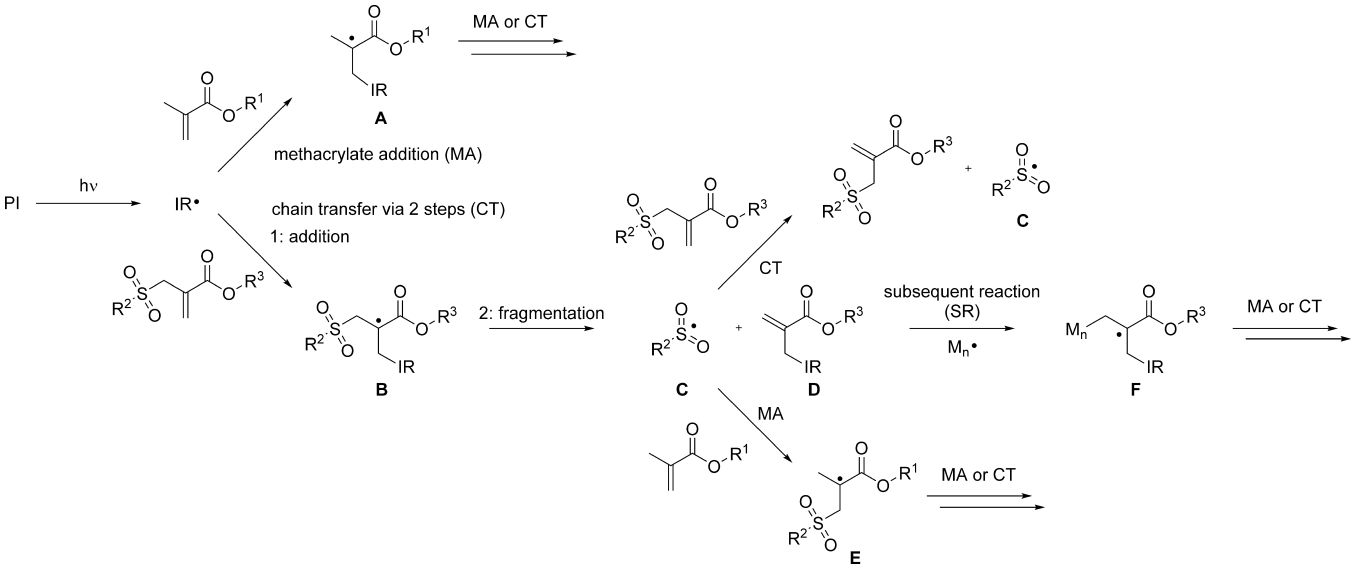
RESULTS AND DISCUSSION

Synthesis. Prior to investigating the novel networks, the β-allyl sulfone precursors had to be synthesized (Scheme 1). The synthesis was performed in three reaction steps, and due to the light sensitivity of the intermediate iodine compounds, it was carried out in a light-protected laboratory (light with wavelengths below 480 nm was filtered). The reagent pTSI was prepared in a simple reaction of sodium p-toluenesulfinate and iodine in an ethanol/water mixture.[30,31]

For the first reaction step, depending on the desired product, 1 equiv (for MAS) or 2 equiv (for DAS) of pTSI was added to

dx.doi.org/10.1021/ma501550b | Macromolecules XXXX, XXX, XXX−XXX

Scheme 2. Photopolymerization Mechanism of a β-Allyl Sulfone-Based Methacrylate System



a solution of dry CH_2Cl_2 and DEGEMA (1 equiv for MAS) or TTEGDMA (1 equiv for DAS).[32,33] The reactions were exposed to visible light and monitored via ^{1}H NMR spectroscopy by looking at the decrease of double bond signal (δ = 6.08 and 5.53 ppm) and the formation of the iodine compound I (δ = 4.47 and 3.90 ppm; d; ^2J = 13.8 Hz). Triethylamine (Et_3N) was added to deprotonate the iodine compound and consequently cleave off the iodine to yield the kinetic product K. The reaction mixture was refluxed overnight to form the desired thermodynamically stable β-allyl sulfones (AS). Purification of both products was achieved by silica gel column chromatography. MAS and DAS were isolated in a satisfactory yield of 56% and 70%, respectively (Figure 2).

Reactivity of β-Allyl Sulfones. To explore the reactivity of the β-allyl sulfones in photopolymerizations, laser flash photolysis (LFP) was employed to determine the addition rate constant of initiator radicals to the double bond. For these experiments, the monofunctional MAS as well as the monomers DEGEMA and MMA were used. Furthermore, it was attempted to determine the follow-up kinetics of the β-scission of intermediate radical B (Scheme 2). For these experiments the initiator Ivocerin was not employed because of two significant disadvantages: (1) the very fast addition kinetics[34] near the limit of the experimental setup and (2) exhibiting transient absorption below 360 nm. The latter being problematic because sulfonyl radicals exhibit a λ_{max} at ~330 nm[35] (Figure S1). Therefore, a bisacylphosphine oxide PI (CGI403) was used. The phosphinoyl radical from this initiator only exhibits weak absorption at lower wavelengths because of the nonaromatic substituent at the central phosphorus.[36]

After photoexcitation at 355 nm the addition rate constant of the phosphinoyl radical P$^\bullet$ (Figure S2) to monomer and AFCT reagent was measured by following the decay of the absorption at 450 nm. Figure 3 shows the dependence of the observed (pseudo-first-order) rate constant on the concentration of reagent.

The addition rate constants (k_{add}) are (2.84 ± 0.04) × 10^7 and (3.84 ± 0.08) × 10^7 M^{-1} s^{-1} for MAS and DEGEMA, respectively. This is also comparable to the addition rate constant of MMA (k_{add} = (3.99 ± 0.06) × 10^7 M^{-1} s^{-1}). It can

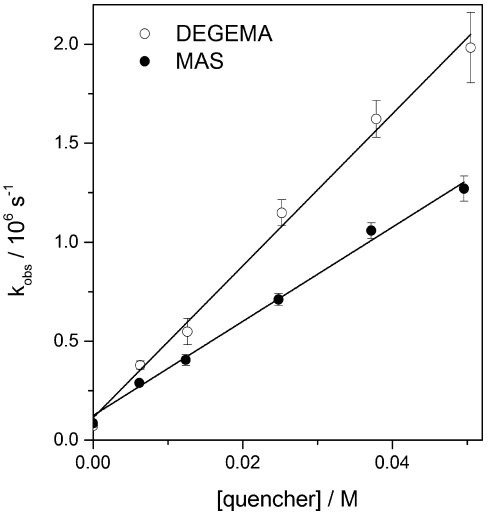


Figure 3. Pseudo-first-order decay rate constant (k_{obs}) of the phosphinoyl radical P$^\bullet$ versus monomer concentration; LFP measured in acetonitrile at ambient temperature.

be seen that the reactivity of the MAS is in a similar range as the methacrylate, but importantly slightly slower.

As is clear from the transient spectra, recorded at different delays after irradiation (Figure 4), there is a second species visible in the spectrum with a λ_{max} at ~315 nm. This peak is attributed to radical B (Scheme 2) resulting from the addition of P$^\bullet$ to MAS. This is further evident when comparing the two decays at 345 and 450 nm. To extract the kinetics for the decay of the second species, global analysis of the complete spectrum was performed. This was necessary as the phosphinoyl radical shows some absorption overlapping with the target radical and the expected sulfonyl radical exhibiting a similar absorption spectrum.

The resulting rate constant for the decay of the second species is (5 ± 1) × 10^4 s^{-1}. This is in the comparable range for sulfonyl β-scission of a tertiary radical next to an ester group, which was determined to be 2 × 10^4 s^{-1}.[37] However, it has to be noted though that this rate constant exhibits a dependence on concentration of MAS. This is probably caused by the

dx.doi.org/10.1021/ma501550b | Macromolecules XXXX, XXX, XXX–XXX

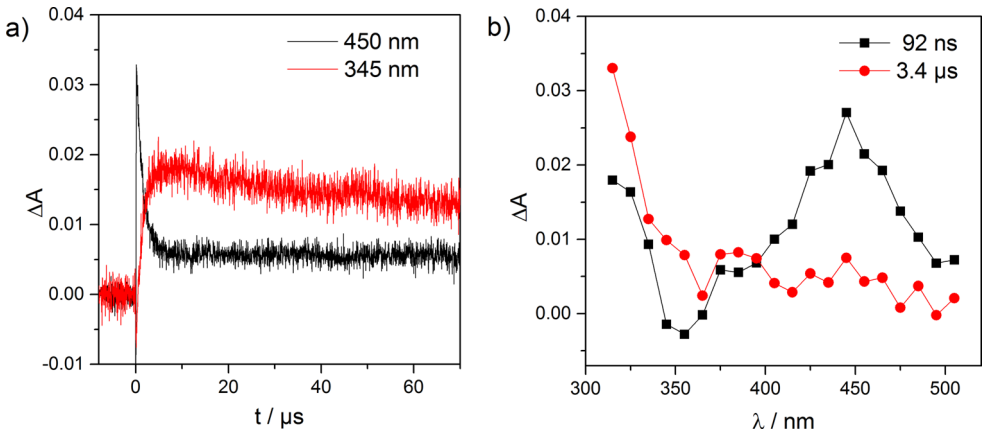


Figure 4. (a) Kinetics of the transient absorptions after laser flash and (b) transient absorption spectra at different delays, of 0.3 mM CGI403 and 25 mM MAS in acetonitrile.

reaction of B with the formed sulfonyl radicals, recombination having to occur because there is no other path available. Additionally, hydrogen abstraction from other MAS molecules will lead to an increase in the observed decay rate of the radical B.

When comparing the determined rate constants to the typical rates of polymerization of methacrylates ($<10^3$ M^{-1} s^{-1}),[38] β-scission is expected to be the major pathway of reaction without significant contributions of homopolymerization or addition reactions before cleavage occurs. Moreover, sulfonyl radicals are very reactive toward methacrylates especially ($\sim 1 \times 10^9$ M^{-1} s^{-1}),[39] leading to fast reinitiation of a new radical chain.

Photopolymerization Mechanism of β-Allyl Sulfones with Methacrylates. In Scheme 2, the mechanism for a mixed chain growth/step growth-like β-allyl sulfone-based methacrylate network formation is shown, similar to how it is proposed for various AFCT reagents in the literature.[15,16,24]

After the formation of initiating radicals (IR$^\bullet$), which are generated by exciting a PI (germanium-based Ivocerin in this case), the radicals can potentially attack either a methacrylate double bond (methacrylate addition, MA) or the double bond of a β-allyl sulfone (chain transfer, CT). The ensuing steps are dependent upon which of the two events takes place. After an MA step, the new radical A can either again undergo a standard radical chain growth step (MA) or participate in a CT step. However, by attacking an AFCT reagent, the CT step is consequently guiding the polymerization mechanism in a step growth-like manner. In the case of a CT step, the growing radical chain will be terminated by forming an intermediate radical B that undergoes fragmentation and forms a sulfonyl radical C and a new double bond (compound D). This sulfonyl radical has again two options. When undergoing a CT step, which results in an event that has the same products as starting materials, this event will continue in a "sulfonyl radical exchange mechanism", until a methacrylate double bond is attacked by the sulfonyl radical. The MA step leads to a propagating radical E that also has the option to perform either an MA or a CT step. It has to be noted that one subsequent reaction (SR) can take place during this polymerization event. After a β-allyl sulfone has reacted, a new, sterically hindered methacrylate-like double bond remains (compound D). During the network formation this double bond can potentially be attacked by any existing radical, for example a radical of a growing polymer chain $M_n^\bullet$, leading to an additional MA step which increases cross-linking in the network. However, according to the literature,[40] SR has a negligible effect on molecular weight regulation. Furthermore, the resulting tertiary radical F has low reactivity and could have a negative effect on the reaction rate.

To elucidate the proposed mechanistic steps and provide estimation for the ratios of MA vs CT during the β-allyl sulfone/dimethacrylate network formation, polymerization experiments of the monofunctional AFCT reagent MAS (20 DB, DB = double-bond equivalents) in the monofunctional DEGEMA (Figure 5) have been performed.

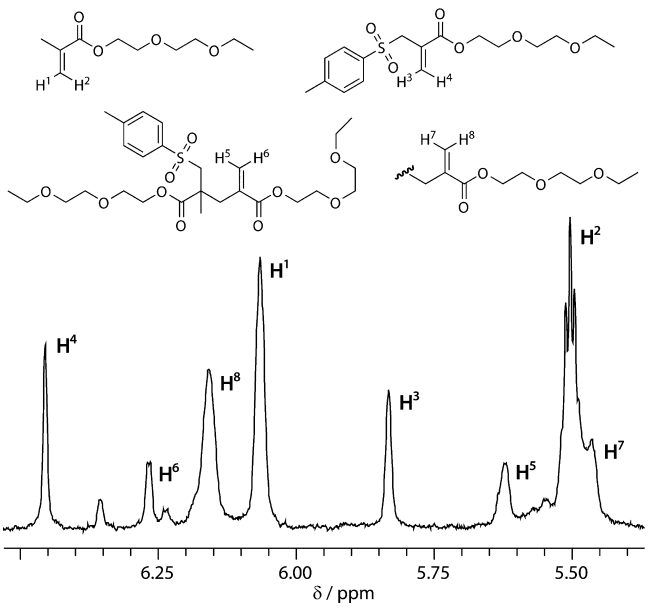


Figure 5. ^{1}H NMR of 20 DB MAS in DEGEMA after photopolymerization with 3 mol % Ivocerin (5 min, 1 W cm^{-2}, 400−500 nm).

When MAS (20 DB) is mixed with DEGEMA and 3 mol % of PI Ivocerin and then irradiated by UV-light (400−500 nm, 1 W cm^{-2}), the resulting polymer can be analyzed based on the photo-DSC plots and by ^{1}H NMR experiments. As a result, the conversion of the different double bonds (MA, CT, and SR) could be determined. Figure 5 represents a polymer sample of a DEGEMA/MAS 20 DB formulation after irradiation of 5 min with the photo-DSC. The double bond hydrogens of the monomer DEGEMA (H^1 and H^2) and the AFCT reagent MAS

dx.doi.org/10.1021/ma501550b | Macromolecules XXXX, XXX, XXX−XXX

(H^3 and H^4) are displayed in the ^{1}H NMR spectrum as well as the hydrogens of the newly formed double bonds (H^{5-8}). The decrease of the H^1 and H^2 integrals gives the yield of the MA step, and the CT step is quantified by the decrease of the H^3 and H^4 integrals. The conversion of the newly formed double bonds (SR step) was determined by monitoring the decrease of the H^{5-8} integrals. The ^{1}H NMR integrals for the double bond signals of DEGEMA (H^{1-2}), MAS (H^{3-4}), and the newly formed double bonds (H^{5-8}) are evaluated after set time intervals of irradiation and correlated to the start integral of the respective double bond signals to yield the double bond conversions (DBCs). As reference, the signals of the aromatic hydrogens originating from MAS are used. The reference integral, for calculating DBC of the SR step, was always set to be equivalent to the decrease of the double bond signals for MAS, with the assumption that for every CT step a new double bond is formed (β-scission is the major pathway).

Multiple experiments have been performed with different irradiation periods, and in Figure 6 and Table S2 the evolution

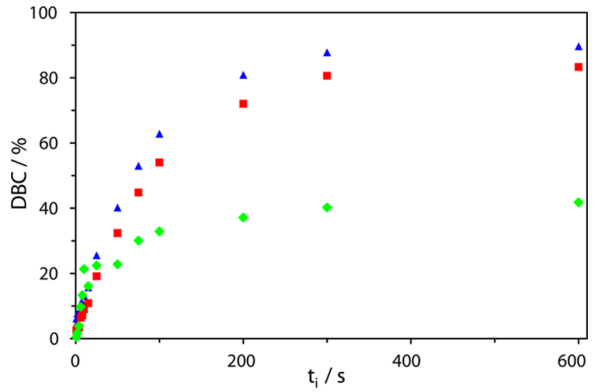


Figure 6. Graphical evolution of DBC for MA (▲), CT (■), and SR (♦) versus irradiation time.

of the DBCs is illustrated. It shows how methacrylate and β-allyl sulfone react very efficiently with each other and are consumed in a similar rate over the whole irradiation period of t_i = 600 s which might enable the formation of a homogeneous network. The experiment shows that the MA reaction is slightly preferred. Nevertheless, it was shown that β-allyl sulfones are very potent AFCT reagents (DBC > 80%) and exhibit good reactivity in a radical copolymerization reaction with methacrylates. It needs to be stated that the conducted experiment hints to the proposed photopolymerization mechanism and reflects the ratios of MA to CT in cross-linking dimethacrylate networks. However, the mobility of the polymer chains decreases significantly during a dimethacrylate photopolymerization, where the gel point is rapidly reached, and this can lead to a significant change in kinetics and the ratio of MA to CT and SR, respectively. Moreover, by photopolymerizing the samples up to a higher conversion, the kinetics and the ratio of MA to CT can change significantly. Through the ^{1}H NMR experiments only the overall conversions of each double bond for this specific system can be determined.

In the following chapters the focus will shift to β-allyl sulfone-based dimethacrylate networks, which cannot be analyzed via ^{1}H NMR spectroscopy due to insolubility. Therefore, the DBC of the tested monofunctional formulation (DEGEMA/MAS 20 DB) should be calculated by means of photo-DSC. The unknown heat of polymerization of each reaction step (MA, CT, and SR) needed to be evaluated from photo-DSC experiments with the help of ^{1}H NMR spectroscopic measurements. Photo-DSC plots (600 s) of pure DEGEMA and a DEGEMA/MAS 20 DB formulation were analyzed (Figure S3). By integrating the photo-DSC plots of the DEGEMA homopolymerization (ΔH_{DEGEMA}) and looking at the corresponding ^{1}H NMR spectra of the polymers (DBC_{NMR}), the theoretical heat of polymerization for DEGEMA ($\Delta H_{0,DEGEMA}$) could be calculated (eq 1) as 60 kJ mol^{-1}, which is in good agreement with literature (62 kJ mol^{-1}).[41]

$$\Delta H_{0,DEGEMA} = \frac{\Delta H_{DEGEMA}}{DBC_{NMR}} \quad (1)$$

$$DBC_{photo\text{-}DSC} = \frac{\Delta H_{DEGEMA}}{\Delta H_{0,DEGEMA}\frac{m_{DEGEMA}}{m_{tot}}} \quad (2)$$

Table 1. Experimental DBC Values Determined via Photo-DSC and NMR

formulation	ΔH_{DEGEMA} (J g^{-1})	$DBC_{photo\text{-}DSC}$ (%)	DBC_{NMR} (%)
DEGEMA	282		95
DEGEMA/MAS (20DB)	191	93	90

The DBC for DEGEMA in a DEGEMA/MAS 20 DB formulation was determined by NMR spectroscopy to be DBC_{NMR} = 90%. Given this value, the theoretical heat coming from the MA step can be calculated to be 185 J g^{-1}, which is very close to the measured value of 191 J g^{-1}. This means that the excess heat (6 J g^{-1}), which amounts to only 3% of the total heat, can be attributed to the CT and SR steps. With this calculation the assumptions were made that the CT step is energy neutral and that the developed heat of the side reactions can be neglected.[40] Taking into account that only 80 mol % in a DEGEMA/MAS 20 DB formulation are methacrylate double bonds, the theoretical heat of polymerization ($\Delta H_{0,DEGEMA}$) needs to be corrected by the weight fraction of DEGEMA (mass of DEGEMA m_{DEGEMA} divided by the total mass of the formulation m_{tot}). With eq 2 the DBC of DEGEMA in a DEGEMA/MAS formulation could be calculated via photo-DSC (Table 1, $DBC_{photo\text{-}DSC}$) and is 93%. The correlation between $DBC_{photo\text{-}DSC}$ and DBC_{NMR} is satisfactory, and the slightly larger value of $DBC_{photo\text{-}DSC}$ can be attributed to side reactions such as SR, which lead to a slightly larger value for ΔH_{DEGEMA} in the calculation. Consequently, this approximation can be used for cross-linking systems to indicate the DBC where ^{1}H NMR spectroscopic analysis is not an option.

Photoreactivity of β-Allyl Sulfone-Based Dimethacrylate Formulations. β-Allyl sulfone-based dimethacrylate formulations potentially delay a photopolymerization reaction by driving the polymerization process toward a mixed chain growth/step growth-like manner. The dimension of this delay and the potential increase in DBC through gel point delay should be investigated. Therefore, the photoreactivity of dimethacrylate formulations with AFCT reagents in various amounts and functionality was investigated by the means of photo-DSC (Table 2 and Figure S4). A pure dimethacrylate formulation of UDMA and D3MA (1/1 molar ratio, 2M) was examined as reference resin for network A. This reference formulation was compared with the formulations for networks

dx.doi.org/10.1021/ma501550b | Macromolecules XXXX, XXX, XXX–XXX

Table 2. Photo-DSC Results of Polymerized Formulations

network	composition	ΔH (J g^{-1})	DBC (%)	$t_{95\%}$[a] (s)
A	2M	223	74	70
B	2M/MAS (16.67 DB)	179	82	105
C	2M/MAS (20 DB)	173	84	114
D	2M/MAS (25 DB)	160	86	128
E	2M/DAS (16.67 DB)	187	83	99
F	2M/DAS (20 DB)	181	85	104
G	2M/DAS (25 DB)	167	86	109

[a] $t_{95\%}$ = time until 95% of reaction heat has been developed.

B-G (2M with 16.67, 20, and 25 DB of monofunctional transfer agent MAS and the difunctional DAS, respectively). A mixture of 2M with 25 DB MAS for instance indicates that 25% of all double bonds in the formulation are double bonds from the respective AFCT compound (MAS), and the remaining double bonds in the formulation are methacrylate double bonds from 2M. For all samples 0.97 mol % Ivocerin were used as PI and the photopolymerization experiments were carried out under a N_2 atmosphere in an isothermal mode at 25 °C. The samples were irradiated for 5 min each (1 W cm^{-2} at the tip of the light guide, 400−500 nm), and the resulting DSC plots were analyzed with respect to their exothermic heat evolution and reaction time. The heat of polymerization (ΔH) for the dimethacrylate homopolymerization of network A is higher compared to the heat of polymerization with AFCT reagents added. For the network A based on 2M the DBC can be determined by dividing the measured ΔH through the theoretical heat of polymerization ($\Delta H_{0,2M}$ = 299.54 J g^{-1}). $\Delta H_{0,2M}$ is calculated using molecular weight ($M_{w,D3MA}$ = 310.43 g mol^{-1}, $M_{w,UDMA}$ = 470.56 g mol^{-1}) and theoretical enthalpy ($\Delta H_{0,D3MA}$ = 120 kJ mol^{-1}, $\Delta H_{0,UDMA}$ = 100 kJ mol^{-1})[42,43] of D3MA and UDMA. In theory, the reaction heat of the CT step should be close to 0, and following this assumption the DBC of the experiments with AFCT reagent added can be determined by correction of $\Delta H_{0,2M}$ according the weight percent (wt %) of 2M in each formulation (m_{2M} = mass of 2M; m_{tot} = total mass of the formulation; eq 3). The reference formulation, solely based on dimethacrylates, forms the network A with a DBC of 74%. The addition of mono- (MAS) or difunctional β-allyl sulfones (DAS) results in a higher DBC of up to 86% with a content of 25 DB MAS and DAS, respectively. Pure dimethacrylate-based photopolymers sometimes suffer from low DBC, which is due to the early gelation and the corresponding decreased mobility of the growing polymer chains. From these results, it can be seen that AFCT reagents increase the DBC of methacrylates (Table 2).

$$\mathrm{DBC}_{2M} = \frac{\Delta H_{2M}}{\Delta H_{0,2M}\frac{m_{2M}}{m_{tot}}} \tag{3}$$

The time where 95% ($t_{95\%}$) of the reaction heat has been developed can be seen as a measure for the rate and progress of the photopolymerization. Overall, the reference monomer mixture A (only dimethacrylates) shows the fastest polymerization with a $t_{95\%}$ of 70 s. The β-allyl sulfone-based dimethacrylate resins exhibit less photoreactivity in contrast to the reference A. The overall reaction takes longer by a factor of max 1.8 (formulations D vs A), which is tolerable

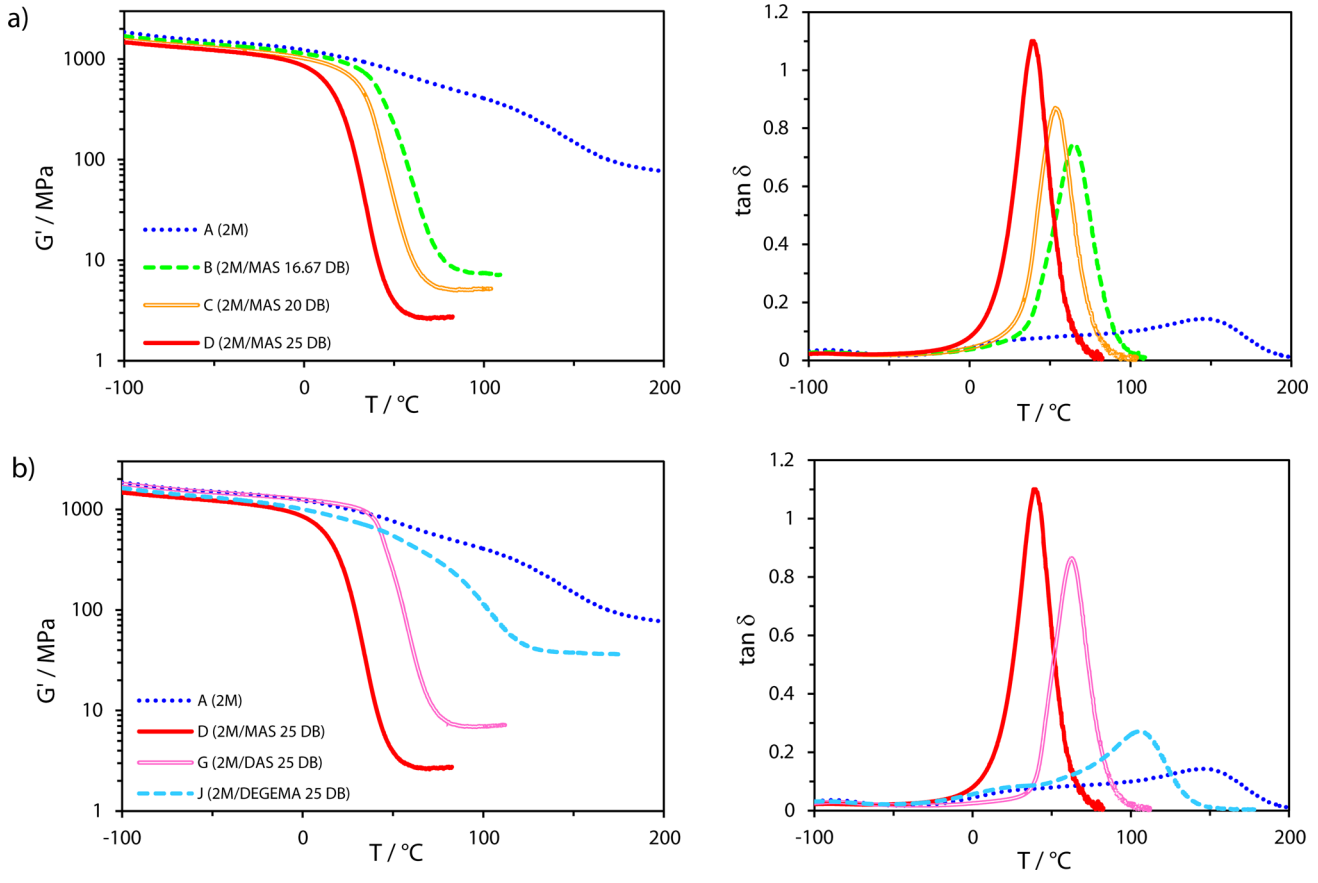


Figure 7. Storage modulus (left) and loss factor curves (right) of different networks.

dx.doi.org/10.1021/ma501550b | Macromolecules XXXX, XXX, XXX−XXX

considering the much more substantial retardation effect of other potential chain transfer reagents such as, e.g., RAFT reagents.[44]

Glass Transition Temperature (T_g) and Rubber Modulus of Elasticity (E_r). It was proposed that by adding β-allyl sulfone to a dimethacrylate formulation the polymer network architecture can be altered leading to more defined and tunable thermal transitions. In order to test the thermal transitions of the synthesized materials, they were characterized by dynamic mechanical thermal analysis (DMTA). An additional standard UV-photopolymerized methacrylate network with 25 DB monomethacrylate DEGEMA (network J) was also analyzed supplementary to network A as reference. Usually, monofunctional methacrylates are used as reactive diluents to tune the viscosity of the photopolymerizable resins. Additionally, the mechanical and thermal properties such as the T_g or E_r can be influenced. Figure 7 shows the resulting curves of the DMTA measurements.

In Figure 7a (storage modulus and loss factor plots), the novel β-allyl sulfone-based dimethacrylate networks with monofunctional AFCT reagent MAS (16.67, 20, and 25 DB; B−D) are compared to the reference network A. As can be seen in Table 3, the thermal glass transition of the networks B−D shows a considerably lower T_g (65−39 °C) and the width of the peak (full width at half-maximum values, fwhm) decreases with increasing AFCT reagent content (30−25 °C). The E_r of A (at $T > T_g$; minimum of storage modulus, 76 MPa) is significantly higher compared to the rubber moduli of B−D with 7, 5, and 3 MPa. This is mainly due to the higher cross-linked, but yet less homogeneous network. Consequently, in the case of β-allyl sulfone/dimethacrylate networks the T_g can be tuned by the increase of AFCT content, while also achieving a narrow glass transition. Importantly, the modulus below glass transition is not changed significantly. In Figure 7b (storage modulus and loss factor plots) the β-allyl sulfone-based networks are compared to the standard dimethacrylate network A and network J containing reactive diluent DEGEMA instead of an AFCT reagent. The networks based on monofunctional MAS exhibit a lower T_g (65−39 °C) and fwhm (30−25 °C) compared to the difunctional DAS-based networks (T_g = 83−63 °C; fwhm = 33−26 °C), although the same amount of active AFCT groups is present in the formulations. This can be rationalized as DAS has the potential to act as a cross-linker, whereas MAS can be considered a reactive diluent. Reference network J does not have a sharp thermal transition (fwhm = 56 °C), which shows that monofunctional methacrylates as diluents do not enable easy tuning of the network properties comparably to the β-allyl sulfones. The sharpness of the glass transition cannot be adequately tuned because the resulting polymer network does not have enhanced homogeneity compared to the new β-allyl sulfone-based polymer networks.

Table 3. DMTA Results of Measured Networks

network	composition	T_g (°C)	fwhm (°C)	E_r (MPa)
A	2M	148		76
B	2M/MAS (16.67 DB)	65	30	7
C	2M/MAS (20 DB)	53	25	5
D	2M/MAS (25 DB)	39	25	3
E	2M/DAS (16.67 DB)	83	33	13
F	2M/DAS (20 DB)	73	29	10
G	2M/DAS (25 DB)	63	26	7
J	2M/DEGEMA (25 DB)	106	56	36

Swellability and Network Density. The swellability and gel fraction of a polymer network correspond to its network density.[45,46] By swelling polymer disks of the tested networks A−J (3 disks per network), the swellability (S) and gel fraction (G) were determined (eqs 4 and 5).

$$S = \frac{m_{swollen}}{m_{dry}} \tag{4}$$

$$G = \frac{m_{dry}}{m_{start}} \tag{5}$$

The disks were weighed at the beginning (m_{start}) and then submerged in ethanol for 7 days. After the swelling period the polymer samples were weighed in the swollen state ($m_{swollen}$) and then dried in a vacuum oven to receive the dry mass of the disks (m_{dry}). This experiment together with the T_g of the photopolymers gives information about the network density of the polymer networks and helps to understand the concept of β-allyl sulfone/dimethacrylate networks. As reference networks, the 2M-based dimethacrylate network A and networks H−J with added monofunctional methacrylate DEGEMA are analyzed. The standard deviations for swellability values and for the gel fraction were <0.8% and <0.4%, respectively, for all measurements.

Table 4. Gel Fraction and Swellability of Polymer Networks Correlated with T_g

network	composition	swellability (wt %)	gel fraction (wt %)	T_g (°C)
A	2M	3.6	98.6	148
B	2M/MAS (16.67 DB)	17.0	98.1	65
C	2M/MAS (20 DB)	18.7	97.0	53
D	2M/MAS (25 DB)	22.4	93.4	39
E	2M/DAS (16.67 DB)	5.9	98.8	83
F	2M/DAS (20 DB)	9.0	97.9	73
G	2M/DAS (25 DB)	11.4	97.5	63
H	2M/DEGEMA (16.67 DB)	6.3	98.9	
I	2M/DEGEMA (20 DB)	7.6	98.9	
J	2M/DEGEMA (25 DB)	9.8	98.5	106

Generally, the gel fraction (98.1−93.4%) of the synthesized β-allyl sulfone/dimethacrylate networks is slightly less than for the reference networks A and H−J (98.9−98.5%). Network D with the highest content of monofunctional AFCT reagent shows the lowest gel fraction (93.4%), which can be explained by the migration of unreacted MAS and the less cross-linked network with the lowest T_g influencing the network mobility already at the experiment temperature. Networks B, C, and E−G still have a high gel fraction (>97%) and a lower and more homogeneous network density compared to network A, which can be concluded by the increase in swellability of the networks B−G. Although pure methacrylate networks with monofunctional DEGEMA as reactive diluents (H−J) have also increased swellability and exhibit comparable gel fraction as dimethacrylate networks with AFCT content, the T_g is much higher and the glass transition broader as can be seen with network J. This shows that with the addition of β-allyl sulfones as AFCT reagents to dimethacrylate formulations a new tool for tuning the network properties and architecture of highly cross-linked photopolymer networks could be established.

dx.doi.org/10.1021/ma501550b | Macromolecules XXXX, XXX, XXX−XXX

CONCLUSIONS

We have introduced a new concept to control the polymer network formation in the radical photopolymerization of dimethacrylates. A mono- and difunctional β-allyl sulfone were successfully synthesized. The AFCT mechanism and reactivity were investigated by LFP, employing the monofunctional β-allyl sulfone. Additionally, photo-DSC and ^{1}H NMR spectroscopic experiments with a monofunctional β-allyl sulfone-based methacrylate formulation were conducted. With the help of those mechanistic studies a CT step paving the way for regulated structures and contributing no significant reaction heat was confirmed. Moreover, it was shown that β-allyl sulfones are good AFCT reagents for methacrylate systems because their addition rate constants are in the same order of magnitude and β-scission is the major pathway for the CT step. The synthesized β-allyl sulfone/dimethacrylate networks have been evaluated toward their photoreactivity (photo-DSC), thermal and mechanical properties (DMTA), and swellability. As expected, the photoreactivity is slightly reduced by the addition of β-allyl sulfones as AFCT reagents. However, the photopolymerization times are still acceptable, prolonging the polymerization only by a factor of <2 for 25 DB monofunctional MAS added to the dimethacrylate formulation. The double-bond conversion in dimethacrylate networks could be improved, which was confirmed by photo-DSC. It was shown that the thermal and mechanical properties of the resulting polymers can be tuned by changing content and functionality of the AFCT reagent. An increasing content of AFCT reagent in a monomer formulation resulted in more homogeneous networks leading to a decrease in T_g (148 °C → 83−39 °C) and significant sharpening of the glass transition (>50 °C → 33−25 °C) of the formed polymer network. Swellability tests have elucidated the relationship between gel fraction, swellability, and network density. β-Allyl sulfone/dimethacrylate networks have lower network density (S = 5.9−22.4 wt %) compared to the corresponding pure dimethacrylate networks (S = 3−6 wt %) but still represent a significantly high gel fraction (>98% for DAS and >93% for MAS). Generally, β-allyl sulfone-based dimethacrylate networks could potentially lead to a number of favorable properties such as low shrinkage stress, high impact resistance, or the ability of acting as covalent adaptable networks (e.g., shape memory polymers). Those assumptions and a comparison with similar thiol−ene networks will be addressed with conclusive studies in the near future.

ASSOCIATED CONTENT

Supporting Information

LFP spectrum of tosyl radical; photo-DSC plots for DEGEMA and 2M networks; viscosity information for storage stability. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: robert.liska@tuwien.ac.at (R.L.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support by the Christian Doppler Research Association, the company Ivoclar Vivadent AG (Liechtenstein), and the P2M network of the ESF is gratefully acknowledged. The authors thank TU Graz/NAWI Graz for the use of the LFP equipment. The authors also thank TU Wien for support in the framework of Lion 2+.

REFERENCES

(1) Fouassier, J.-P. *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*; Hanser: Munich, 1995; p 388 ff.
(2) Studer, K. *Coating* **2007**, *40* (9), 33−37.
(3) Abe, Y. *DIC Technol. Rev.* **2005**, *11*, 1−20.
(4) Fleischer, J. E. *Mod. Paint Coat.* **2001**, *91* (4), 21−22 25..
(5) Parrott, M. C.; Luft, J. C.; Byrne, J. D.; Fain, J. H.; Napier, M. E.; DeSimone, J. M. *J. Am. Chem. Soc.* **2010**, *132* (50), 17928−17932.
(6) Dworak, C.; Koch, T.; Varga, F.; Liska, R. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48* (13), 2916−2924.
(7) Mautner, A.; Qin, X.; Kapeller, B.; Russmueller, G.; Koch, T.; Stampfl, J.; Liska, R. *Macromol. Rapid Commun.* **2012**, *33* (23), 2046−2052.
(8) Mautner, A.; Qin, X.; Wutzel, H.; Ligon, S. C.; Kapeller, B.; Moser, D.; Russmueller, G.; Stampfl, J.; Liska, R. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51* (1), 203−212.
(9) Fedorovich, N. E.; Swennen, I.; Girones, J.; Moroni, L.; van Blitterswijk, C. A.; Schacht, E.; Alblas, J.; Dhert, W. J. A. *Biomacromolecules* **2009**, *10* (7), 1689−1696.
(10) Husar, B.; Heller, C.; Schwentenwein, M.; Mautner, A.; Varga, F.; Koch, T.; Stampfl, J.; Liska, R. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49* (23), 4927−4934.
(11) Torgersen, J.; Ovsianikov, A.; Mironov, V.; Pucher, N.; Qin, X.; Li, Z.; Cicha, K.; Machacek, T.; Liska, R.; Jantsch, V.; Stampfl, J. *J. Biomed. Opt.* **2012**, *17* (10), 105008/1−105008/10.
(12) Torgersen, J.; Qin, X.-H.; Li, Z.; Ovsianikov, A.; Liska, R.; Stampfl, J. *Adv. Funct. Mater.* **2013**, *23* (36), 4542−4554.
(13) Liska, R.; Schwager, F.; Cano-Vives, R.; Stampfl, J. *Polym. Prepr.* **2004**, *45* (2), 77−78.
(14) Yakacki, C. M.; Shandas, R.; Safranski, D.; Ortega, A. M.; Sassaman, K.; Gall, K. *Adv. Funct. Mater.* **2008**, *18* (16), 2428−2435.
(15) Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49* (5), 1079−1131.
(16) Yagci, Y.; Reetz, I. *React. Funct. Polym.* **1999**, *42* (3), 255−264.
(17) Bowman, C. N.; Fairbanks, B. D.; Cramer, N. B.; Anseth, K. S. *Polym. Prepr.* **2010**, *51* (2), 703−704.
(18) Hoyle, C. E.; Bowman, C. N. *Angew. Chem., Int. Ed.* **2010**, *49* (9), 1540−1573.
(19) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (21), 5301−5338.
(20) An, L.; Gao, C.; Yan, X.; Fu, Z.; Yang, W.; Shi, Y. *Colloid Polym. Sci.* **2012**, *290* (8), 719−729.
(21) Meijs, G. F.; Rizzardo, E.; Thang, S. H. *Polym. Bull.* **1990**, *24* (5), 501−505.
(22) Park, H. Y.; Kloxin, C. J.; Abuelyaman, A. S.; Oxman, J. D.; Bowman, C. N. *Macromolecules* **2012**, *45* (14), 5640−5646.
(23) Hutson, L.; Krstina, J.; Moad, C. L.; Moad, G.; Morrow, G. R.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2004**, *37* (12), 4441−4452.
(24) Sato, E.; Uehara, I.; Horibe, H.; Matsumoto, A. *Macromolecules* **2014**, *47* (3), 937−943.
(25) Popielarz, R. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34* (17), 3471−3484.
(26) Tanaka, K.; Yamada, B. *Macromol. Chem. Phys.* **2000**, *201* (14), 1565−1573.
(27) Nair, D. P.; Cramer, N. B.; Scott, T. F.; Bowman, C. N.; Shandas, R. *Polymer* **2010**, *51* (19), 4383−4389.
(28) Kloxin, C. J.; Bowman, C. N. *Chem. Soc. Rev.* **2013**, *42* (17), 7161−7173.
(29) Harvey, I. W.; Phillips, E. D.; Whitham, G. H. *Tetrahedron* **1997**, *53* (18), 6493−6508.
(30) Edwards, G. L.; Muldoon, C. A.; Sinclair, D. J. *Tetrahedron* **1996**, *52* (22), 7779−7788.

(31) Liu, L. K.; Chi, Y.; Jen, K.-Y. *J. Org. Chem.* **1980**, *45* (3), 406−410.
(32) Batra, D.; Shea, K. J. *Org. Lett.* **2003**, *5* (21), 3895−3898.
(33) da Silva, C. C. M. M.; Fleming, M. D. C. M.; Oliveira, M. A. B. C. S.; Garrido, E. M. J. *J. Chem. Soc., Perkin Trans. 2* **1994**, No. 9, 1993−2000.
(34) Neshchadin, D.; Rosspeintner, A.; Griesser, M.; Lang, B.; Mosquera-Vazquez, S.; Vauthey, E.; Gorelik, V.; Liska, R.; Hametner, C.; Ganster, B.; Saf, R.; Moszner, N.; Gescheidt, G. *J. Am. Chem. Soc.* **2013**, *135* (46), 17314−17321.
(35) Ho, H. T.; Ito, O.; Iino, M.; Matsuda, M. *J. Phys. Chem.* **1978**, *82* (3), 314−19.
(36) Jockusch, S.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120* (45), 11773−11777.
(37) Timokhin, V. I.; Gastaldi, S.; Bertrand, M. P.; Chatgilialoglu, C. *J. Org. Chem.* **2003**, *68* (9), 3532−3537.
(38) Moad, G.; Solomon, D. H. *The Chemistry of Radical Polymerization*; Elsevier: Amsterdam, 2006; p 218 ff.
(39) Chatgilialoglu, C.; Mozziconacci, O.; Tamba, M.; Bobrowski, K.; Kciuk, G.; Bertrand, M. P.; Gastaldi, S.; Timokhin, V. I. *J. Phys. Chem. A* **2012**, *116* (29), 7623−7628.
(40) Miyake, K.; Zetterlund, P. B.; Yamada, B. *Macromol. Rapid Commun.* **2004**, *25* (22), 1905−1911.
(41) Dainton, F. S.; Ivin, K. J.; Walmsley, D. A. G. *Trans. Faraday Soc.* **1960**, *56*, 1784−92.
(42) Ganster, B.; Fischer, U. K.; Moszner, N.; Liska, R. *Macromol. Rapid Commun.* **2008**, *29* (1), 57−62.
(43) Ganster, B.; Fischer, U. K.; Moszner, N.; Liska, R. *Macromolecules* **2008**, *41* (7), 2394−2400.
(44) Fenoli, C. R.; Wydra, J. W.; Bowman, C. N. *Macromolecules* **2014**, *47* (3), 907−915.
(45) Pavlinec, J.; Moszner, N. *J. Appl. Polym. Sci.* **1997**, *65* (1), 165−178.
(46) Pavlinec, J.; Moszner, N. *J. Appl. Polym. Sci.* **2003**, *89* (3), 579−588.