Research Article

Approaching new biomaterials: copolymerization characteristics of vinyl esters with norbornenes, allyl esters and allyl ethers

Patrick Steinbauer,[a,b,c] Robert Liska[b,c] and Stefan Baudis[a,b,c*] ●

Abstract

Vinyl ester-based monomers for radical photopolymerization have recently been shown to be promising alternatives to (meth)acrylates through lower irritancy and cytotoxicity. Vinyl ester monomers are becoming increasingly important on account of new, more cost-efficient synthetic production methods, not to forget their increased reactivity and improved material properties in combination with thiol–ene polymerization. Due to their biocompatibility and degradability, these monomers are more frequently used in tissue engineering. Nevertheless, the material properties can be improved by possible copolymerizations with other monomers. Therefore, the copolymerization behavior of vinyl ester with norbornene, allyl ether and allyl ester has been studied fundamentally in a photoreactor via free radical photopolymerization. Here, the consumption of double bonds of the monomers has been identified using NMR spectroscopy. Copolymerization parameters have been determined using the Kelen–Tüdős method. Results show equal consumption of vinyl ester and co-monomer double bonds leading to alternating copolymerizations. The double bond conversion was confirmed via *in situ* real-time near-infrared photorheology. Mono- and difunctional vinyl esters with co-monomers have also provided further insight into the polymer network of these copolymers.
© 2021 The Authors. *Polymer International* published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

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

Keywords: photopolymers; vinyl ester copolymers; Kelen–Tüdős; RT-NIR photorheology; photoreactor

INTRODUCTION

Free radical photopolymerization occurs in many industrial sectors for photochemical curing.[1] Monomers based on (meth) acrylates are known for their reactivity in free radical polymerization and thus are widely employed. They are beneficial in dental fillings, adhesives, protective coatings, inks and stereolithography.[2] Reasons for the versatility of photoinducible radical polymerization of (meth)acrylates are fast curing rates and spatial resolution, solvent-free formulations, high storage stability and room temperature operations.[3] Mechanical properties of polymers can be tuned via different spacer units and (meth)acrylates as reactive diluents.[4,5] Nevertheless, these functional groups have several drawbacks such as irritancy and cytotoxicity as well as related environmental issues.[6–8] These are attributed to the reactivity of the acrylate double bond to Michael addition reactions with amine or thiol groups of proteins or DNA.[9] Besides monomer toxicity, degradation products in biological systems have potential to be harmful. Here poly[(meth)acrylic acid] can be formed. Several approaches to reduce the cytotoxicity of monomers using vinyl ester (VE) moieties have been proposed.[10] Some years ago the first research groups started to work with VEs.[9–12] However, this is still limited today, although VEs have a low cytotoxicity

and corresponding degradation products are transformed to poly(vinyl alcohol) or acetaldehyde.[13] Nevertheless, autocatalytic bulk erosion could be exhibited upon degradation of poly(vinyl ester)s. But the formed acid molecules are of low molecular weight and are easily excreted. One reason for the low interest is the lower reactivity of VEs towards free radical polymerization compared to (meth)acrylates.[9] VE monomers exhibit low monomer reactivity but form very reactive radicals, which allows higher tendency for hydrogen abstractions.[10] Another reason for limited use of VE monomers is the poor availability of commercial VEs, since classical synthesis of VE functionalities requires very expensive catalysts based on toxic mercury salts.[14] These multistep

*   Correspondence to: S Baudis, Technische Universität Wien Getreidemarkt 9/ 163 1060 Vienna, Austria. E-mail: stefan.baudis@tuwien.ac.at

a   Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing, TU Wien, Vienna, Austria

b   Division of Macromolecular Chemistry, Institute of Applied Synthetic Chemistry, TU Wien, Vienna, Austria

c   Austrian Cluster for Tissue Regeneration, Vienna, Austria

reactions are atom inefficient and cost intensive. Previously, Hofecker *et al.*[15] reported a more convenient, more economic and safer synthesis pathway to obtain VEs in sufficient yields. VE homopolymers are very brittle and often break during crosslinking due to high shrinkage stress. To modify the polymer network, chain transfer agents such as thiols are widely used.[16] Lower modulus and sharper glass transition temperature result in shrinkage stress reduction and higher fracture toughness. Therefore, VEs are increasingly associated with free radical thiol–ene chemistry, where reactivity is increased by the formation of highly reactive thiyl radicals.[17–20]

An improvement of mechanical properties and reactivities could result from the copolymerization of VEs, which has not been investigated so far. Strictly alternating copolymers of norbornene and maleic anhydride can be mentioned here, which have been studied in great detail as promising materials for photolithography (193 nm).[21–23] These copolymers can be used for alternative single-layer resist platforms as matrix resins for future microelectronics. The alternating copolymers synthesized by free radical polymerization at higher temperatures (65 °C) have many desirable properties such as good thermal stability, high glass transition temperature, optical transparency, high decomposition temperature, etc. The rigid repeat unit can contribute to useful physical properties.[24,25] Copolymerization of norbornene with ethylene or propylene initiated by metal complexes affords cyclic olefin copolymers with unique properties.[26,27] Furthermore, norbornenes have been copolymerized with methacrylates to achieve useful optical properties.[25]

The radical polymerization of norbornene is not as widespread as ring-opening metathesis polymerization, cationic polymerization or vinyl-type polymerization.[28] The copolymerization of other co-monomers should not be ignored either. Allyl esters have been copolymerized with vinyl acetate at elevated temperatures (60 °C).[29] Additionally, allyl ethers can be copolymerized with maleimide and photoinitiators[30] as well as ethylene using metal catalysts.[31]

We are interested in the modification of VE polymers to obtain materials with improved properties. Here, we report studies of free radical copolymerization of VE with norbornene, allyl ester and allyl ether at room temperature. Kinetic studies for the determination of the copolymerization parameters and investigations of the polymer network are of essential importance for a rational design of new VE-based materials.

MATERIALS AND METHODS

Materials and general methods

Allyl ethyl ether (>95.0%; TCI Chemicals), diallyl adipate (>95.0%, TCI Chemicals), 1,2-di(allyloxy)ethane (>95%, abcr), *N,N*-dimethylformamide (DMF; 99.8%, Sigma Aldrich), divinyl adipate (>99.0%, TCI Chemicals), 1,6-hexanediol (99%, Sigma Aldrich), 5-norbornene-2-carboxylic acid (endo/exo mixture; TCI Chemicals), oxalyl chloride (>98.0%, Sigma Aldrich), triethylamine (>99.0%, Sigma Aldrich) and vinyl hexanoate (>99.0%, TCI Chemicals) were purchased and used without further purification. The photoinitiator bis(4-methoxybenzoyl) diethylgermane (Ivocerin®) was kindly provided by Ivoclar Vivadent AG. All reagents were used without further purification. Methylene chloride (DCM) was dried using a PureSolv system (Inert Technology, Amesbury, MA, USA). ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker Avance DRX-400 FT-NMR spectrometer. The chemical shift was reported in ppm (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Deuterated chloroform ($CDCl_3$, 99.5% deuteration, Eurisotop Cambridge, UK) was used as solvent. Analysis of the spectra was performed with the software Mestre-Nova 14.1.0-24037.

Silica column chromatography was performed with a Büchi MPLC system equipped with a control unit (C-620), fraction collector (C-660), refractive index detector and UV photometer (C-635). As stationary phase, Merck silica gel 60 (0.040–0.063 mm) was used.

Photoreactor studies

For the photoreactor studies, five different molar ratios (3:1, 3:2, 1:1, 2:3, 1:3) of vinyl ester (VEst) and norbornene (Norb), allyl ester (AEst) or allyl ether (AE) were mixed with 4 mol% Ivocerin as photoinitiator. Dimethyl terephthalate (20 wt%) was added as internal standard. An amount of 1 g of this formulation was placed in a 10 mL two-necked round-bottom flask and diluted with 5 mL of benzene-d_6 (99.5% deuteration, Eurisotop Cambridge, UK) as solvent. The solution was purged with argon for 30 min before being irradiated with UV light (Exfo OmniCure S200 broadband Hg lamp with a 400–500 nm filter, 1.5 W cm^{-2} intensity at the tip of the light guide, *ca* 9 mW cm^{-2} on the surface of the sample measured with an Ocean Optics USB 2000+ spectrometer). Samples (0.05 mL) were taken before irradiation (0 s) and after 10, 30, 40, 80, 120, 200, 400, 800, 1200 and 1600 s of irradiation. Gel permeation chromatography (GPC) was conducted with the last sample after 1600 s irradiation. The samples were quenched with 0.5 mL of $CDCl_3$ and ^{1}H NMR spectra were recorded. The conversion was calculated from the integral ratio between the double bond signals before irradiation and after the defined periods of time. The aromatic signals at 8 ppm and the —CH_3 signals at around 4 ppm of dimethyl terephthalate were used as external standard.

Gel permeation chromatography

GPC measurements were performed using a Malvern Viscotek TDA system equipped with a Viscotek TDA 305-021 RI+ viscodetector, a U detector module 2550 for TDA 305, and a Viscotek SEC-MAL 9 light scattering detector. Samples were prepared in 2 mg mL^{-2} tetrahydrofuran (THF) solutions spiked with 0.5 mg mL^{-1} butylated hydroxytoluene as flow marker and syringe-filtered (200 nm PTFE syringe filters). GPC measurements were carried out with three consecutive PSS SDC columns (100, 1000 and 100 000 Å) using dry THF as mobile phase at a flow rate of 0.8 mL min^{-1} and a temperature of 35 °C. Conventional calibration was conducted with 11 narrow polystyrene standards (M_w = 0.375–177 kDa) supplied by PSS. Analysis was performed with OmniSEC V5.12.461 software (Malvern).

Synthesis of 5-norbornene-2-carbonyl chloride (Norb-Cl)[32]

A three-neck round-bottom flask was equipped with a dropping funnel and was charged with argon. To the flask were added oxalyl chloride (24 mL, 280 mmol, 4 eq.), DCM (10 mL) and DMF (0.1 mL). The dropping funnel was filled with 5-norbornene-2-carboxylic acid (6.5 mL, 70 mmol, 1 eq.) and 40 mL of DCM. The flask was cooled with ice and after stirring for 15 min the solution in the dropping funnel was slowly added to the oxalyl chloride solution. The ice bath was removed and the reaction mixture was stirred at room temperature for 24 h. After evaporation of DCM and oxalyl chloride, the residual was distilled at 6 mbar and 47 °C to afford 8.5 g (78% of theory) of Norb-Cl as colorless liquid. ^{1}H NMR (400 MHz,

CDCl$_3$, δ): 6.32–6.17 (m, 1H, CH=CH endo/exo), 6.17–5.99 (m, 1H, CH=CH exo/endo), 3.49–2.71 (m, 3H, CH), 2.07–1.87 (m, 1H, CH$_2$, CH$_2$ bridge), 1.57–1.38 (m, 2H, CH$_2$, CH$_2$ bridge), 1.37–1.28 (m, 1H, CH$_2$, CH$_2$ bridge). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 175.19 (s, C=O), 139.17 (s, CH=CH exo), 138.83 (s, CH=CH endo), 135.02 (s, CH=CH exo), 131.75 (s, CH=CH endo), 56.56 (s, CHC=O endo), 56.45 (s, CHC=O exo), 49.36 (s, CH$_2$ bridge), 47.29 (s, CH endo), 47.03 (s, CH exo), 46.43 (s, CH$_2$ bridge), 43.00 (s, CH endo), 42.00 (s, CH exo), 31.29 (s, CH$_2$ exo), 30.21 (s, CH$_2$ endo).

Synthesis of 6-(5-norbornen-2-ylcarbonyloxy) hexyl 5-norbornene-2-carboxylate (bisNorb)

Norb-Cl (3 eq., 14 g, 90 mmol) in DCM (50 mL) was added drop-wise to a mixture of 1,6-hexanediol (1 eq., 3.5 g, 30 mmol) and triethylamine (3 eq., 12.5 mL, 90 mmol) in DCM (130 mL) at 0 °C under argon atmosphere. The reaction was stirred overnight. The white precipitate was filtered, the residue was washed with brine (3 × 100 mL) and the solvent was evaporated. The product was purified through silica flash column chromatography (EE:PE 10:90) to yield 8.8 g (82% of theory) of a colorless viscous liquid. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.52–5.74 (m, 4H, 2× CH=CH endo/exo), 4.16–3.84 (m, 4H, —OCH$_2$), 3.51–3.08 (m, 2H, 2× CH), 3.05–2.76 (m, 4H, 2× CH + 2× COCH), 2.23–1.03 (m, 16H, 2× CH$_2$, 2× CH$_2$ bridge, 4× CH$_2$ alkyl). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 176.18 (s, 2× C=O endo/exo), 137.98 (s, 2× CH=CH exo), 137.68 (s, 2× CH=CH endo), 135.72 (s, 2× CH=CH exo), 132.30 (s, 2× CH=CH endo), 64.28 (s, 2× —OCH$_2$ exo), 64.03 (s, 2× —OCH$_2$ endo), 49.58 (s, 2× CH$_2$ bridge endo), 46.57 (s, CHC=O exo), 46.32 (s, 2× CH$_2$ bridge exo), 45.67 (s, CHC=O endo), 43.30 (s, 2× CH endo), 43.14 (s, 2× CH exo), 42.49 (s, 2× CH endo), 41.59 (s, 2× CH exo), 30.29 (s, 2× CH$_2$ exo), 29.15 (s, 2× CH$_2$ endo), 28.57 (s, 2× CH$_2$ alkyl), 25.61 (s, 2× CH$_2$ alkyl).

Real-time near-infrared (RT-NIR) photorheology

An Anton Paar MCR 302 WESP rheometer with a P-PTD 200/GL Peltier glass plate, an H-PTD 200 heating hood and a PP25 measuring system was used to conduct the RT-NIR photorheology experiments. The rheometer was coupled with a Bruker Vertex 80 Fourier transform infrared spectrometer to analyze the chemical conversion over time of the sample. Details of the setup and the measurement procedure are described in the literature.[33] In the course of every single measurement, the exact amount of monomer formulation (150 µL) was pipetted at the center of the glass plate. The measurements were conducted at 25 °C with a gap of 200 µm. The formulations were oscillated with a strain of 1% and a frequency of 1 Hz. UV light was used to initiate the reaction, which was emitted via an Exfo OmniCure™ 2000 device with a broadband Hg lamp (300, 400–500 nm, 1 W cm^{-2} at the tip of the light guide, ca 10 mW cm^{-2} on the surface of the glass plate, measured with an Ocean Optics USB 2000+ spectrometer). The vinyl ester, norbornene, allyl ester and allyl ether double bond conversions (DBCs) were determined by recording a set of single spectra (time interval of ca 0.26 s) with OPUS 7.0 software. The respective double bond bands were integrated at ca 6194 cm^{-1} (VEst), ca 6020 cm^{-1} (Norb), ca 6124 cm^{-1} (AEst) and ca 6122 cm^{-1} (AE). In the case of peak overlapping, PeakFit software (v4.12) was used for peak deconvolution. The ratio of the double bond peak area at the start of UV light irradiation and at the end of the measurement gave the DBC. All measurements were performed in triplicate with satisfactory reproducibility.
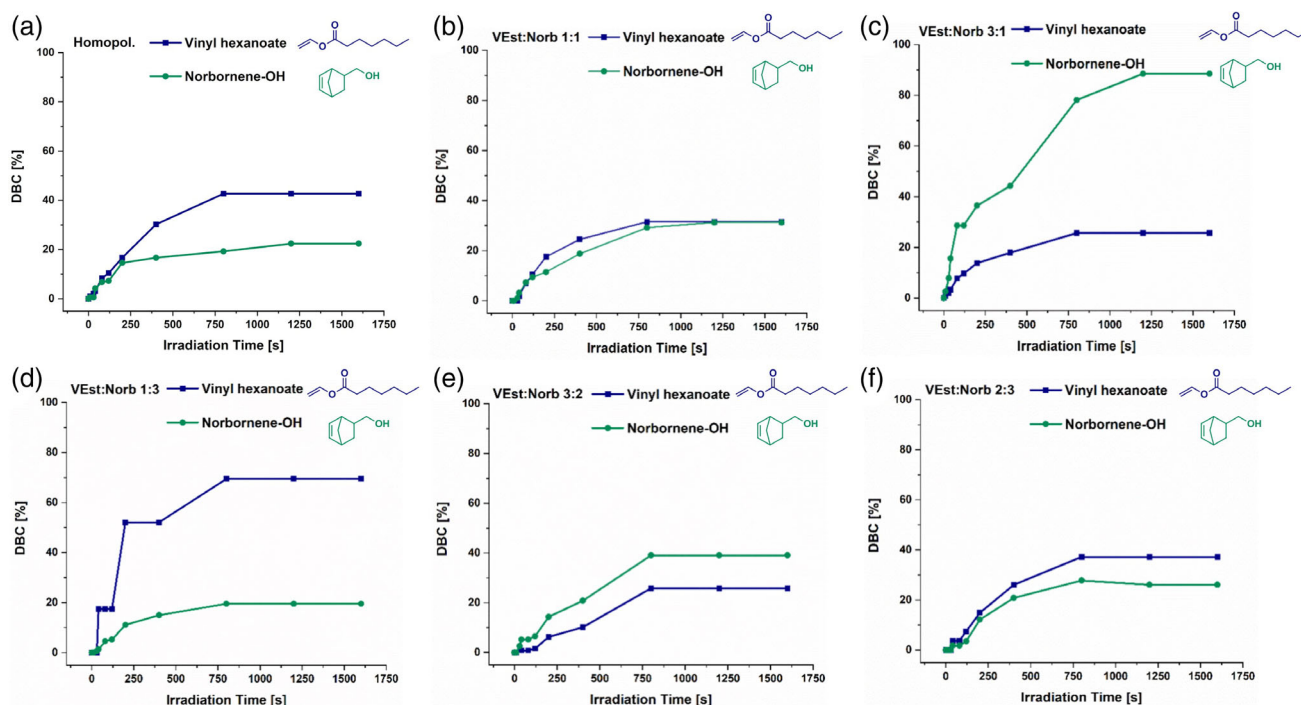
RESULTS AND DISCUSSION

Copolymerization study of vinyl ester with various co-monomers

Studies of free radical copolymerization of VEst with Norb, AEst and AE were conducted at room temperature. The Alfrey–Price Q–e scheme attempts to combine resonance and polarity considerations in copolymerizations.[34] According to this theory, the monomers used (VEst, Norb, AEst, AE) have low Q values and high negative e values. They are all classified in group III in the Q–e scheme. These monomers have poor resonance stabilizing radicals. According to theory, copolymerization of monomers in the same group would be feasible. To corroborate this, photoreactor studies followed by photorheology studies were performed.

Photoreactor

To investigate the copolymerization behavior of vinyl ester with norbornene, allyl ester and allyl ether, kinetic studies via a photoreactor were conducted. Mixtures of seven different molar ratios of the monofunctional vinyl hexanoate (VEst) and monofunctional co-monomers 2-hydroxymethylnorbornene (Norb), allyl hexanoate (AEst) and allylethylether (AE) were prepared within a photoreactor using deuterated benzene as solvent, dimethyl terephthalate as external standard and Ivocerin as photoinitiator. The formulation was irradiated (broadband Hg lamp, 800 s, 400–500 nm, ca 9 mW cm^{-2} on the surface of the sample) and samples were taken after set time intervals. Figure 1(A) illustrates a DBC of 43% during homopolymerization of VEst after 800 s of irradiation time. This rather low value compared to bulk polymerization with 4 mol% photoinitiator ensues from the diluting effect of the solvent. The polymerization of Norb shows a DBC of 22%. Janiak and Lassahn[35] stated that the result of cationic or radical polymerization of norbornene is a low-molar-mass oligomeric material with 2,7-connectivity of the monomer. In general, little is known about free radical polymerization of norbornenes. There is also the possibility of leaving the bicyclic structural unit intact and only attacking double bond of the π-component.[36] The reactivity of the norbornene double bond was evaluated to be favored for attack from the exo side.[37] Further studies predicted a nonplanar double bond with hydrogens in endo direction.[38,39] However, an NMR study confirms that norbornenes cannot undergo radical homopolymerization without catalysts. Two formulations of Norb were prepared and the conversion was calculated via ^{1}H NMR. The DBC decreased at lower content of Ivocerin (supporting information, Table S1) and subsequent liquid chromatography–mass spectrometry measurement of the cured formulations demonstrated that after hydrogen abstraction by the initiator, norbornene dimers were formed. As a result, the DBC of 22% of Norb is accomplished via formation of dimers or trimers of norbornene units. In addition, GPC measurements were performed to observe the molecular weight and distribution during polymerization. Table S2 (supporting information) evidences significantly higher molecular weight of the vinyl hexanoate homopolymer and the lowest molecular weight of the norbornene polymerization. This again corroborates the formation of dimers or trimers. Moreover, the VEst–Norb photoreactor study includes the polymerization behavior of vinyl hexanoate with Norb in five different molar ratios (1:1, 1:3, 2:3, 3:1, 3:2) (Figs 1(B)–(F)). Figure 1 (B) illustrates almost equal consumption and DBC of VEst (■)

Polym Int 2021   © 2021 The Authors.   wileyonlinelibrary.com/journal/pi

Polymer International published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

3

Figure 1. (A) Homopolymerization study of vinyl hexanoate (VEst) (■) and 2-hydroxymethylnorbornene (Norb) (●). (B–F) Copolymerization study of VEst (■) with Norb (●) in the photoreactor for various molar ratios of VEst:Norb: (B) 1:1, (C) 3:1, (D) 1:3, (E) 3:2 and (F) 2:3.

and Norb (●) at a molar ratio of 1:1 (VEst:Norb). However, the molecular weight is not nearly as high as that of the homopolymer (supporting information, Table S1). In Fig. 1(C) the ratio was changed to 3:1 (VEst:Norb), which resulted in 78% DBC of Norb (●), but 19.5% DBC of VEst (■). Hence, the VEst double bond was consumed as long as Norb was present. After the consumption of Norb, VEst was no longer able to homopolymerize. Similar behavior was found for the ratio 3:2 (VEst:Norb) (Fig. 1(E)). Figures 1(D) and (F) show the opposite behavior because of a greater proportion of Norb in the formulation (1:3 and 2:3 VEst:Norb).

Here, Norb is equally consumed as long as free VEst double bonds are present. The rather low molecular weight of these polymers is related to termination via norbornene as seen in the GPC data (supporting information, Table S2). Indeed, norbornene groups have a pronounced terminating effect; still, the conversion of VEst is at an acceptable level, even with an excess of Norb. The copolymerization parameters were calculated using the proportions of VEst and Norb in the polymers of five different molar ratios. The Kelen–Tüdös method was used, due to higher conversions of about 15% (see Eqn (1)):

$$\eta = \frac{\frac{[M_1]}{[M_2]} \times \frac{m_2}{m_1} \times \left(\frac{m_1}{m_2} - 1\right)}{\alpha + \frac{[M_1]^2}{[M_2]^2} \times \frac{m_2}{m_1}} \text{ and } \xi = \frac{\frac{[M_1]^2}{[M_2]^2} \times \frac{m_2}{m_1}}{\alpha + \frac{[M_1]^2}{[M_2]^2} \times \frac{m_2}{m_1}} \quad (1)$$

with $\alpha > 1$ as random definable constant, M_1 and M_2 as amount of substance fraction in monomer and m_1 and m_2 as amount of substance fraction in the polymer. The variable ξ can take values between 0 and 1. By plotting η against ξ, a straight line is obtained, which provides the ordinate section ($-r_2/\alpha$) and the copolymerization parameter r_1 at $\xi = 1$. For the polymerization of VEst and Norb, $r_1 = 0$ and $r_2 = 0$ were determined (supporting information, Fig. S1).

The copolymerization diagram shows a horizontal line and the monomer ratio of 1:1 is the azeotropic point (supporting information, Fig. S1A). The results of these two parameters indicate a strictly alternating copolymerization (supporting information, Fig. S1B). The parameters are presented in Table 1. Similar photoreactor studies with VEst and AEst as well as AE were performed in the same five ratios and homopolymerizations as mentioned above (supporting information, Figs S2 and S4). The results of DBC$_{end}$ and GPC analysis are summarized in Tables S3 and S4 (supporting information). The same trend as with the copolymerization of VEst and Norb can be followed. Molar ratio 3:1 (VEst with AEst or AE) showed the highest molecular weight. In contrast to the VEst–Norb system, more double bonds were consumed in the VEst–AEst and VEst–AE systems. At 1:1 feed, both double bonds were equally consumed. Copolymerization parameters of these systems were calculated via the Kelen–Tüdös method (Figs S3 and S5). The parameters are summarized in Table 1. VEst showed strictly alternating radical copolymerization with Norb and AEst. The copolymerization with AE is alternating but not strictly.

Table 1. Copolymerization parameters of vinyl hexanoate (VEst) with 2-hydroxymethylnorbornene (Norb), allyl ester (AEst) and allylethylether (AE)

Copolymerization	r_1[a]	r_2[a]
VEst + Norb	0.032	0.039
VEst + AEst	0.005	0.011
VEst + AE	−0.006	0.002

[a] Determined via the Kelen–Tüdös method.

4
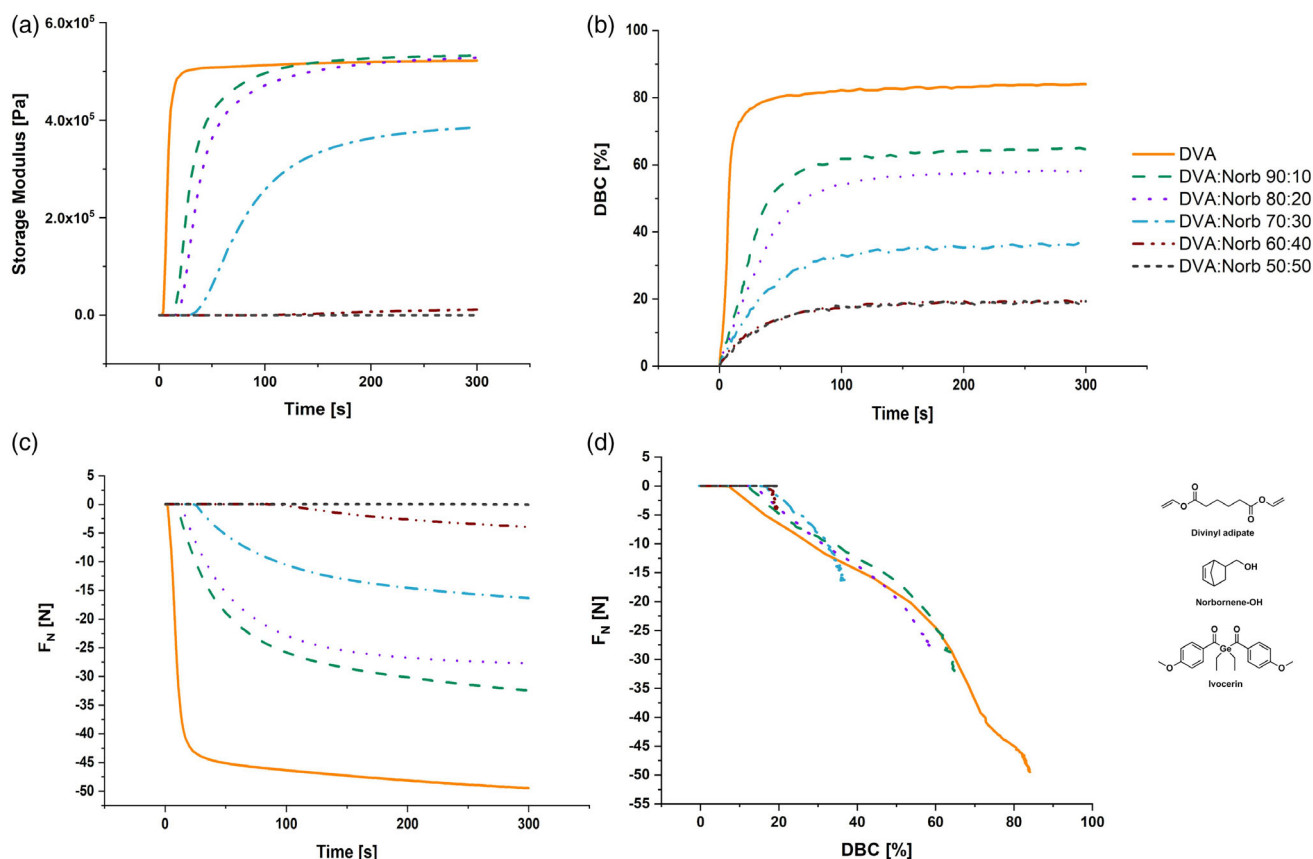
Figure 2. RT-NIR photorheology of DVA with different ratios of Norb. (A) Storage modulus over time, (B) DBC over time, (C) shrinkage force (F_N) plot and (D) shrinkage force–DBC plot.

RT-NIR photorheology

The photoreactor studies for a monofunctional system exhibit copolymerization of VEst with Norb, AEst and AE, but to gain further insight into network formation, RT-NIR photorheology was performed. Here, the DBC via NIR spectroscopy and rheological data during photopolymerization can be determined via *in situ* measurement. RT-NIR photorheology is a powerful tool for tracking several important parameters while curing.[33] The time until gelation (t_{Gel}), intersection of storage modulus G' and loss modulus G'', conversion at gel point (DBC_{Gel}), the final DBC, the time when 95% of the final storage modulus is reached ($t_{95,G'}$), the final storage modulus (G'_{Final}) and the final shrinkage stress (normal force, $F_{N,Final}$) give more insight into a photopolymerization reaction and the ensuing polymer network.

The difunctional vinyl ester divinyl adipate (DVA) was mixed in different molar ratios (90:10 ≈ 11 db% of co-monomer, 80:20 ≈ 25 db%, 70:30 ≈ 43 db%, 60:40 ≈ 66 db%, 50:50 mol % ≈ 100 db%) with Norb, AEst and AE in the presence of 1 mol % Ivocerin and was measured via photorheology. The results of DVA:Norb formulations were compared to neat DVA (solid, orange) (Fig. 2). Additionally, DVA was formulated with vinyl hexanoate (supporting information, Fig. S6 and Table S5) for comparison. Norb exhibits higher delay of t_{Gel} than vinyl hexanoate in a DVA mixture (supporting information, Table S6). From a molar ratio of 80:20 (corresponds to 25 db% of Norb) on, the storage modulus deteriorates due to increasing termination by norbornene (see Fig. 2(A)). The neat DVA with Ivocerin exhibits high shrinkage force and 25 db% of Norb (*ca* 80:20) can reduce the

shrinkage stress markedly from 50 to 28 N at constant storage modulus (Fig. 2(B)).

Figure 2(C) illustrates that higher ratio of Norb leads to a decrease in DBC, which results in shrinkage force reduction. This is also supported by the data in Fig. 2(D), where a shrinkage force reduction (with respect to the DBC) is only observed in the initial phase of the polymerization. Table S6 summarizes all recorded parameters of RT-NIR photorheology with DVA and Norb. The DBC_{Gel} of the vinyl ester increased from 7% to 13% (80:20 VEst: Norb) at constant storage modulus. Nevertheless, the final DBC decreases markedly from 84% to 58%. The DBC_{Gel} and DBC_{final} of DVA and Norb are not significantly different. There is equal consumption of both functional groups. The results corroborate the copolymerization behavior of VEst and Norb. With higher feed of Norb, more termination and recombination occurred. Photorheology measurements of DVA and AEst show a drop of storage modulus at a molar ratio of 50:50 (DVA:AEst) (supporting information, Fig. S7A). The addition of AEst (60:40 DVA:AEst) leads to shrinkage force reduction of 6 N (supporting information, Fig. S7B). Here, the DBC_{final} is constant and exhibits equal consumption of both double bonds (supporting information, Fig. S7C). The polymerization of DVA and AE showed behavior similar to that of Norb. Storage modulus is constant until a ratio of 70:30 (DVA:AE) (supporting information, Fig. S8A) and leads to a shrinkage force reduction of 10 N (supporting information, Fig. S8B). The shrinkage reduction is caused by a decrease in DBC_{final}. The results of both copolymerizations are summarized in Tables S7 and S8 (supporting information).

To gain further insight into the polymer network of the copolymerization of VEst with Norb, AEst and AE, a difunctional photorheology study was conducted with DVA and bisNorb, diallyladipate (diAEst) and 1,2-di(allyloxy)ethane (diAE) with the same ratios as before. At a ratio of 90:10 (DVA:bisNorb), the gel point was delayed and the storage modulus was increased compared to DVA (supporting information, Fig. S9). Shrinkage force was reduced as DBC decreased. If the concentration of Norb is too high, termination is more likely to occur. The copolymerization is also confirmed in Table S11 (supporting information), since the Norb and DVA double bonds were consumed equally. The photorheology study with DVA and diAEst shows an increase or at least constant storage modulus compared to pure DVA at all ratios (supporting information, Fig. S10 and Table S10). Up to a feed of 70:30, the shrinkage is significantly reduced while the DBC_{final} remains unchanged. Both double bonds are consumed equally. The polymerization of DVA and diAE proceeds in a manner similar to that of DVA and bisNorb (supporting information, Fig. S11 and Table S11).

CONCLUSIONS

The behavior during free radical photopolymerization of vinyl ester with norbornene, allyl ester and allyl ether was investigated in fundamental kinetic studies via photoreactor experiments. NMR spectroscopy showed equal consumption of vinyl ester and co-monomer double bonds. Once the vinyl ester double bonds were consumed, termination occurred because co-monomers were not able to homopolymerize. However, after full consumption of co-monomer, some double bonds were still converted via homopolymerization of the vinyl ester. Using five different ratios of vinyl ester and co-monomer, copolymerization parameters were determined via the Kelen–Tüdös method. In all three cases, r_1 and r_2 showed values around zero, which indicates alternating copolymerization, since the other monomer is preferentially incorporated into the polymer. Equal consumption of vinyl ester and co-monomer was confirmed with DBC_{Gel} and DBC_{end} values via RT-NIR photorheology in addition to the photoreactor experiments. With increasing concentrations of co-monomer norbornene, increased termination and recombination behavior was observed. Photorheology measurements of DVA with monofunctional norbornene showed the same storage moduli until a ratio of 80:20 (DVA:Norb) compared to pure DVA. But high storage moduli were exhibited with allyl ether and allyl ester co-monomers until 60:40 (DVA:AEst) and 50:50 (DVA:AE). The higher the feed of co-monomer, the lower the DBC, which results in a shrinkage force reduction. Photorheology experiments with DVA and difunctional co-monomers intensify these effects and results. With a ratio of 80:20 (DVA:bisNorb or DVA:diAE) the storage modulus drops due to increasing termination and recombination behavior. However, the results for DVA:diAEst show equal storage moduli until a ratio of 50:50 in comparison to pure DVA. Considering the ratios of vinyl ester and co-monomer with the same storage moduli as pure DVA and then studying the shrinkage force of these, a significant shrinkage force reduction can be seen.

Since vinyl esters are used more frequently in materials for medical applications, this basic study should identify new copolymers and their type of radical copolymerization resulting in different microstructures. The considered copolymerizations of vinyl esters with different co-monomers could lead to new polymers with improved mechanical properties in the near future. The synthesis of vinyl esters and co-monomers as well as resulting copolymers with improved mechanical properties is planned, for example, for 3D printing.

SUPPORTING INFORMATION

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

REFERENCES

1 Fouassier J-P, *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*. Carl Hanser Verlag, Munich (1995).
2 Liska R, Schuster M, Inführ R, Turecek C, Fritscher C, Seidl B et al., *J Coat Technol Res* **4**:505–510 (2007).
3 Nichol JW, Koshy ST, Bae H, Hwang CM, Yamanlar S and Khademhosseini A, *Biomaterials* **31**:5536–5544 (2010).
4 Schuster M, Turecek C, Kaiser B, Stampfl J, Liska R and Varga F, *Macromol Sci A* **44**:547–557 (2007).
5 Schuster M, Turecek C, Mateos A, Stampfl J, Liska R and Varga F, *Monatsch Chem* **138**:261–268 (2007).
6 Calnan CD, *Contact Dermatitis* **6**:53–54 (1980).
7 Andrews LS and Clary JJ, *J Toxicol Environ Health* **19**:149–164 (1986).
8 Heller C, Schwentenwein M, Russmüller G, Koch T, Moser D, Schopper C et al., *J Polym Sci A Polym Chem* **49**:650–661 (2011).
9 Husár B, Heller C, Schwentenwein M, Mautner A, Varga F, Koch T et al., *J Polym Sci A Polym Chem* **49**:4927–4934 (2011).
10 Heller C, Schwentenwein M, Russmueller G, Varga F, Stampfl J and Liska R, *J Polym Sci A Polym Chem* **47**:6941–6954 (2009).
11 Lee TY, Guymon CA, Jonsson ES, Hait S and Hoyle CE, *Macromolecules* **38**:7529–7531 (2005).
12 Lee TY, Kaung W, Jönsson ES, Lowery K, Guymon CA and Hoyle CE, *J Polym Sci A Polym Chem* **42**:4424–4436 (2004).
13 Mautner A, Steinbauer B, Orman S, Russmüller G, Macfelda K, Koch T et al., *J Polym Sci A Polym Chem* **54**:1987–1997 (2016).
14 Lobell M and Schneider MP, *Synthesis (Stuttg)*:375–377 (1994).
15 Hofecker A, Knaack P, Steinbauer P, Markovic M, Ovsianikov A and Liska R, *Synth Commun* **50**:3629–3641 (2020).
16 Mautner A, Qin X, Wutzel H, Ligon SC, Kapeller B, Moser D et al., *J Polym Sci A Polym Chem* **51**:203–212 (2013).
17 Hoyle CE and Bowman CN, *Angew Chem Int Ed* **49**:1540–1573 (2010).
18 Cramer NB, Reddy SK, O'Brien AK and Bowman CN, *Macromolecules* **36**:7964–7969 (2003).
19 Hoyle CE, Yeon LT and Todd R, *J Polym Sci A Polym Chem* **42**:5301–5338 (2004).
20 Cramer NB and Bowman CN. *J Polym Sci A Polym Chem* **39**:3311–3319 (2001). https://doi.org/10.1002/pola.1314
21 Houlihan FM, Wallow TI, Nalamasu O and Reichmanis E, *Macromolecules* **30**:6517–6524 (1997).
22 Pasquale AJ, Long TE, Truong H and Allen RD, *J Adhes* **78**:1–13 (2002).
23 Sanders DP, *Chem Rev* **110**:321–360 (2010).
24 Gmernicki KR, Cameron M and Long BK, *J Polym Sci A Polym Chem* **54**:985–991 (2016).
25 Ihara E, Ishii S, Yokoyama K, Fujiwara Y, Ueda T, Inoue K et al., *Polym J* **45**:606–613 (2013).
26 Ihara E, Honjyo S, Kobayashi K, Ishii S, Itoh T, Inoue K et al., *Polymer (Guildf)*. **51**:397–402 (2010).
27 Yu K-H, Huang S-L, Liu Y-H, Wang Y, Liu S-T, Cheng Y-C et al., *Molecules* **22**:1095 (2017).
28 Janiak C and Lassahn PG, *Macromol Rapid Commun* **22**:479–492 (2001).
29 Shigetomi Y, Kojima T and Ono N, *J Polym Sci A Polym Chem* **28**:3317–3325 (1990).
30 Burget D, Mallein C and Fouassier JP, *Polymer (Guildf)* **44**:7671–7678 (2003).
31 Jian Z and Mecking S, *Angew Chem Int Ed* **54**:15845–15849 (2015).
32 Chae C-G, Yu Y-G, Seo H-B, Kim M-J, Grubbs RH and Lee J-S, *Macromolecules* **51**:3458–3466 (2018).

33 Gorsche C, Harikrishna R, Baudis S, Knaack P, Husar B, Laeuger J *et al.*, *Anal Chem* **89**:4958–4968 (2017).

34 Alfrey T and Price CC, *J Polym Sci* **2**:101–106 (1947).

35 Janiak C and Lassahn PG. The vinyl homopolymerization of norbornene. *Macromol. Rapid Commun.* **22**:479–493 (2001). https://doi.org/10.1002/1521-3927(20010401)22:7<479::aid-marc479>3.0.co;2-c

36 Blank F and Janiak C, *Coord Chem Rev* **253**:827–861 (2009).

37 Spanget-Larsen J and Gleiter R, *Tetrahedron Lett* **23**:2435–2438 (1982).

38 Huisgen R, Ooms PHJ, Mingin M and Allinger NL, *J Am Chem Soc* **102**:3951–3953 (1980).

39 Holthausen MC and Koch W, *J Phys Chem* **97**:10021–10027 (1993).