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Low volume shrinkage of polymers by photopolymerization of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropanes†

Paul Pineda Contreras,‡ Payal Tyagi‡ and Seema Agarwal*

Low volume shrinkage of polymers by photoring-opening polymerization of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (VCP) and its methyl substituted derivate 1,1-bis(ethoxycarbonyl)-2-(prop-1-en-2-yl)-cyclopropane (Me-VCP) is presented. The aim of this study was to evaluate the photopolymerization behavior and structure of the corresponding polymers from VCP and its methyl substituted derivates 1,1-bis(ethoxycarbonyl)-2-(prop-1-en-2-yl)-cyclopropane (Me-VCP) and 1,1-bis(ethoxycarbonyl)-2-methyl-2-(prop-1-en-2-yl)-cyclopropane (DiMeVCP). VCP monomers were polymerized using camphorquinone (CQ) as a photo-initiator either in a binary or ternary photo-initiator system. The binary systems were formulated with ethyl 4-dimethylaminobenzoate (EDMAB) in relation to the monomer and 1 mol% of CQ. The ternary system was a mixture of 1 mol% of CQ, 2 mol% of EDMAB and 2 mol% of DPIHFP. Ternary photo-initiator systems showed high polymerization rates leading to high conversion in a short photo-activation time. One of the important findings is the formation of higher amounts of 1,5-type ring-opened units and lower amounts of cyclobutane-containing units in photopolymerization, which can make VCP an attractive component of dental composites, as the volume shrinkage is proportional to the 1,5-ring opening. Earlier it was observed that thermal free radical polymerization of VCPs gives higher amounts of cyclobutane structures compared to 1,5-type ring-opened units in the corresponding polymers, causing VCP to be excluded from the list of promising dental composites, as the volume shrinkage was higher than expected.

1. Introduction

2-Vinylcyclopropane-1,1-dicarboxylates (VCPs) are attractive monomers as they display less polymerization shrinkage than other vinyl monomers, such as methacrylates.[1–3] This characteristic makes such cyclic monomers attractive as low-shrinking components in dental adhesives or filling composites, curing resins, molding and filling materials. As a consequence, VCPs have attracted considerable interest among researchers in publications and patents.[4–6] Many studies have been carried out to investigate the influence of the type and position of substituents on the rate, molecular weight, volume shrinkage and polymer structure of VCPs by thermal radical polymerization.[7] It has been reported that thermal radical polymerization pro-

vides a polymer consisting of a 1,5-ring opened unit along with a new unit, which is believed to have a cyclobutane structure (Scheme 1).[3]

By comparing the dependence between the shrinkage on polymerization and the reciprocal of the molecular weight of several VCP monomers, a higher shrinkage was observed than expected for ring-opening monomers. Furthermore the obtained volume shrinkage was in the range of vinyl monomers. This additional shrinkage was attributed to the formation of the cyclobutane containing unit during polymerization.[3] But since VCPs are possible ring-opening monomers, they are expected to be useful materials with lower shrinkage in volume, by reducing the formation of cyclobutane containing units during radical polymerization.

It is interesting to note that not many detailed studies in the open literature are provided for ring-opening photo-

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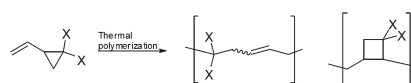
Scheme 1 Reported polymer structures of the radical ring-opening polymerization of VCPs.

polymerization of VCPs. Camphorquinone (CQ) and ethyl-4-dimethylamino-benzoate (EDMAB) and 2,4,6-trimethylbenzoyldiphenyl-phosphinoxide (Lucirin), a three component initiator system was used for photocopolymerization of bifunctional methacrylate monomers like bis-GMA and UDMA with a vinyl-cyclopropane derivate (1,3-bis[[(1-ethoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy)]benzene to form crosslinked networks.[8]

Till now, the practical application of VCPs has been restricted, as in comparison with standard methacrylate monomers they are less reactive.[3,9] However, the research group of N. Moszner *et al.* in particular, has synthesized and investigated with great effort a number of different 1,1-di-substituted VCPs to increase the reactivity during thermal radical polymerization; unfortunately the many different approaches resulted only in moderate improvements.[10] In order to enhance the polymerization reactivity of VCPs regardless, not by synthetic methods, but rather by a variation of the photopolymerization conditions, diaryliodonium salts were introduced to the photo-initiator system. Diaryliodonium salts are efficient photo-initiators for both radical and ionic (mostly cationic) polymerization.[11,12] When light is irradiated on the excited iodonium it decomposes to an aryliodo radical cation, a reactive aryl radical and an anion.[13] However, these salts do not absorb significantly above 300 nm, therefore UV light sources were used, which restrict their biological applications, where UV light is not recommended. However, it was reported that using dyes that absorb in the visible light region as sensitizers, would allow a reaction with the onium salts, promoting the decomposition.[14] In a similar way, onium salts can also act in radical polymerization.[15,16] Several kinds of visible light sensitizer dyes have been investigated, such as camphorquinone,[17] safranine,[18] acridine derivatives[16] and acetophenone dyes.[14] Camphorquinone, a dye widely used as a photo-initiator for radical polymerization, can act as a photo-sensitizer to diphenyliodonium hexafluorophosphate, which does not absorb light in the visible region, improving the reactivity of the photo-initiator system.[17]

The aim of the present work was to study the effect of the photoinitiated ring-opening polymerization of 2-vinylcyclopropane-1,1-dicarboxylate and the corresponding monomethyl substituted VCP on the polymer structure, kinetics and volume shrinkage. Camphorquinone was used as a photosensitizer with ethyl-4-dimethylaminobenzoate for binary, and together with diphenyliodonium hexafluorophosphate, for ternary initiation processes to evaluate the influence of an onium salt on the radical photopolymerization kinetics and polymer structure of VCPs.

2. Experimental section

2.1 Measurements

[1]H- (300 MHz) and ^{13}C- (75 MHz) NMR spectra were recorded on a Bruker Ultrashield-300 spectrometer in CDCl$_3$, using tetramethylsilane (TMS) as an internal standard. GC measurements have been performed by a GC-FID system of the type QP-5050 from Shimadzu Company with nitrogen as carrier gas. GC-MS measurements have been performed with a system Agilent 5977A MSD with helium as carrier gas. Molecular weights and polydispersity index (PDI) of the polymers were determined by GPC with a Knauer system equipped with two columns, PSS-SDV (linear, 10 μl, 60 cm × 0.8 cm), and a differential refractive index (RI) detector. THF was used as an eluent at a flow rate of 0.8 ml min^{-1}. A polystyrene calibration was employed as a reference. A Mettler thermal analyzer of the type 821c DSC was used for the thermal characterization of polymers. DSC scans were recorded under a nitrogen atmosphere at a flow rate of 70 ml min^{-1} at heating rates of 10 K min^{-1}. Each sample weighed about 10 ± 2 mg for DSC analysis. The polymerization shrinkage was calculated from the difference in density of the monomer and the formed polymers (Archimedes principle). The densities of the monomers were measured by a 1 mL pycnometer, and the densities of the polymers, by water displacement of 400 mg cured samples. The polymer samples were prepared by inserting the monomer–initiator mixture into the bottom of a 10 mL standard test tube at light exclusion, flushing the tubes with an argon gas for 30 s and irradiating each sample for 48 h at room temperature. Afterwards the samples were cooled and bounced out of the glass tubes to a glass plate of similar density and weight, as the VCP polymers occurred as not totally solid but rather as viscous polymer melts. The polymerization shrinkage was determined separately for the three samples.

2.2 Materials

1,4-Dibromo-2-butene, diethyl malonate, sodium, isoprene, camphorquinone (CQ) and *tert*-butyl peroxide (DTBP) were supplied by Aldrich and used without further purification. Azo-bisisobutyronitrile (AIBN) was obtained from Bayer AG and recrystallized from methanol before use. Ethyl 4-dimethyl-aminobenzoate (EDMAB) (Fluka) and diphenyliodonium hexafluorophosphate (DPIHFP) (ABCR GmbH & Co. KG) were used without further purification. Tetrahydrofuran (BASF), ethanol (BASF), chloroform and pentane were distilled before use.
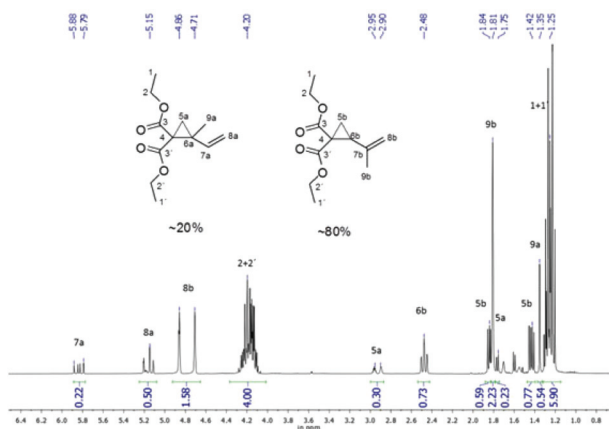
2.3 Monomer synthesis

1,1-Disubstituted 2-vinylcyclopropanes were obtained from diethyl malonate and the corresponding dibromo butane as per the published procedure.[3,19] 1,4-Dibromo-2-methyl-2-butene was prepared previously in a reaction between isoprene and bromine in chloroform (Scheme 2).[20]

The detailed reaction procedures, including purification and characterization, are given in the relevant ESI.† The structures were characterized by NMR and GC. In contrast to the
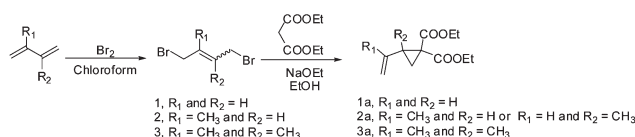
Scheme 2 Schematic pathway to synthesize monomers **1a–3a**.

Fig. 1 ¹H-NMR of the monomer (**2a**), which consists of diethyl 2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (~20%) and diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate (~80%) (CDCl₃, 300 MHz).

reported literature, we observed for the synthesis of **2a** a constitution isomer of around 80 : 20 of diethyl 2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate to diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate, that could not be separated by distillation or column chromatography as shown in the NMR (Fig. 1). Therefore this mixture was used for polymerizations.

2.4 Polymerization

2.4.1 General procedure. The polymerization was carried out in a polymerization tube which was vacuum dried and degassed prior to use. The monomer was introduced into the polymerization tube along with a radical initiator. Different photoinitiator systems were investigated at various levels under stirring conditions: 1 mol% CQ and 2 mol% EDMAB; 1 mol% CQ + 2 mol% EDMAB and DPIHFP at different molar concentrations; 1 mol% CQ and 2 mol% DPIHFP. The light radiation source was a white-light LED lamp (details are given below). For comparison purposes thermal polymerizations were also carried out using 1 mol% DTBP and 1 mol% AIBN. The thermally induced polymerizations were carried out at 70 °C and 120 °C respectively for AIBN and DTBP initiators. The polymerizations were stopped after definite time intervals by freezing the mixture in liquid nitrogen. Afterwards the polymer melts were dissolved in THF and precipitated into cold pentane. The precipitated polymers were filtered and dried in a vacuum oven at room temperature till they achieved a constant weight. The degree of conversion was calculated by the mass difference of the polymer and the monomer. The data were plotted and curve fitting was performed by Hill three parameter non-linear regressions. Using these data, the polymerization rate R_p (min⁻¹) was calculated from the slope of the linear fit.

2.4.2 Radiation source. To perform the monomer photo-activation, a white light lamp of GSVITEC Company (Marathon MultiLED) was used. The lamp head consisted of 25 cells. The power of the lamp was 800 W halogen equivalents (data as per the lamp manual provided by GSVITEC). The emission spec-

trum of the white light LED lamp was recorded by a Shimadzu fluorescence spectrometer RF type 1502. The white-light LED lamp emits primarily at 442 and 540 nm wavelengths. The light emission between 400 and 480 nm (absorption range of CQ) corresponds to 43% of the total emission power of the emitted light of the lamp head.

3. Results and discussion

Thermal radical polymerization of VCPs such as 2-vinylcyclopropane-1,1-dicarboxylates and derivatives is well-studied in the literature.[1,3,7] The radical from the thermal initiator adds at the vinyl double bond of VCP followed by isomerization with ring-opening leading to the formation of a stable t-radical for further propagation. In the present work, photo-polymerization of 2-vinylcyclopropane-1,1-dicarboxylate (**1a**) and the corresponding mono and di-α-methyl substituted VCPs (**2a** and **3a**) was studied using different photo-initiator systems in different ratios (camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (EDMAB) (1 : 2 mol%), and CQ and EDMAB (1 : 2 mol%) with different ratios of DPIHFP as the ternary initiator (1, 2 and 4 mol%)[17] (Scheme 3).

The reaction kinetics of the photo-polymerization with the binary initiator system (1 mol% CQ and 2 mol% EDMAB) is depicted in Fig. 2. White to light yellow colored polymers, which were soluble in common solvents were obtained from
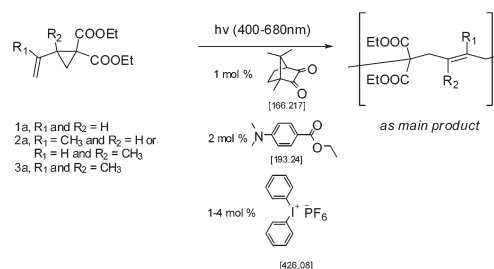
Scheme 3 Schematic polymerization equation of photosynthesized polymers.
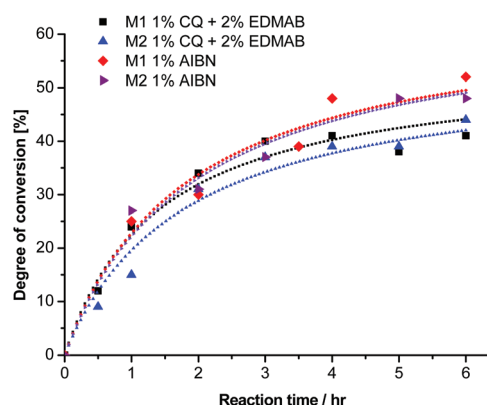
Fig. 2 Degree of conversion for the polymerization of monomers **1a** (M1) and **2a** (M2) with different initiators. Concentrations of 1 mol% CQ and 2 mol% EDMAB as well as 1 mol% AIBN were used.

1a and **2a**. However, **3a** the di-methyl substituted monomer did polymerize only in negligible yields, which confirms the reported literature for thermal polymerization of methyl substituted 1-ethoxycarbonyl-2-vinylcyclopropanes[21] and methyl-substituted 1,1-diethoxycarbonyl-2-vinylcyclopropanes.[19] This trend was explained with the assumption of the higher chain transfer reaction of the di-methyl substituted VCP.[19] Nevertheless it should be considered that the presence of two methyl substituents, one in the α-position and the other on the cyclopropane ring might provide the cause of hyperconjugation, a relative stable radical, whereby the rate of ring-opening is reduced to a range within the radical termination reaction, and becomes a byword of the propagation.

The rates of polymerization (R_p) of the photo-polymerization with the binary initiator system were 0.30 and 0.25% per min for **1a** and **2a**, respectively. As a matter of fact it seemed that by conventional radical polymerization, the radical ring opening process, independent of the radical initiator and α-substituent, was very slow. Therefore for providing a comparison we added in Fig. 2 the thermal polymerization kinetics of **1a** and **2a** in the presence of 1 mol% AIBN, a thermal initiator, where we observed almost identical R_p values of 0.29 and 0.28% per min. These R_p values were still slow, which is in line with the literature.[3,19]

However the ternary photoinitiator system with additional DPIHFP could provide faster vinylcyclopropane polymerizations. It is worth mentioning that the ternary photoinitiator systems are already known to provide enhanced rates of polymerizations to the conventional vinyl monomers owing to an increased concentration of initiating radicals or because of the concurrent cationic or radical initiating species.[16,17,22] The observed R_p values for ring-opening polymerization of VCPs were much higher with higher overall conversions (around 80%) compared to the conventional CQ-EDMAB system. Therefore for a detailed investigation we added DPIHFP as an initiator at different molar concentrations.

We observed for the degree of conversion as a function of the photo-activation time for the ternary initiator system with 2 mol% DPIHFP R_p values of 11.37 and 2.60% per min for **1a** and **2a**, respectively (Fig. 3). Thereby the R_p values, compared
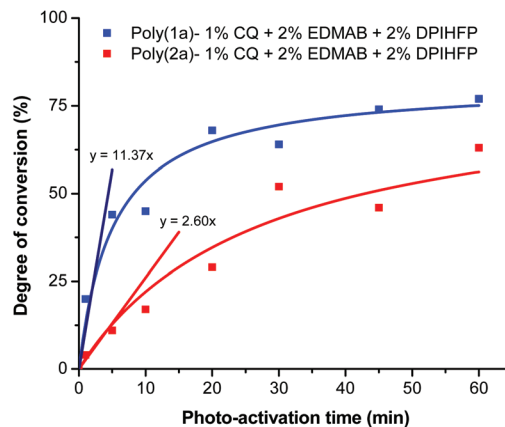
Fig. 3 Degree of conversion for the photo-polymerization of monomers **1a** and **2a** with 1 mol% CQ + 2 mol% EDMAB + 2 mol% DPIHFP as the ternary initiator.

to the conventional photopolymerization system CQ-EDMAB and to the thermal polymerization AIBN (Fig. 2), can be significantly improved by using a ternary system to the factor ~35 and ~10 for poly(**1a**) and by factor ~38 and ~9 for poly(**2a**). In general, an increase in the molar mass of polymers was also seen on using the ternary initiator system (Table 1).

Further the concentration level of DPIHFP within the ternary photo-initiator system showed a significant effect both on the rate of polymerization and the degree of monomer conversion (Fig. 4). Polymerization with a lower concentration of DPIHFP (below 2%) showed higher monomer conversions at low reaction times. 10 min of light radiation and just 0.5 mol% DPIHFP in the ternary initiator system was sufficient to polymerize almost 25% of the monomers. However, for further photo-activation, there was almost no further increment in the yield of polymerization. One of the possible reasons could be that the onium salt decomposes after a certain period of time. The highest conversion was obtained with 4% onium salt concentration (about 80% conversion in 15 minutes), although there were solubility problems with onium salts having a concentration of 2% or higher in 1,1-disubstituted 2-vinylcyclopropanes.

Table 1 Properties of binary and ternary photo- and thermal-polymerized monomers **1a** and **2a**[a]

Entry		Initiator[b]	Temp./°C	Ring opened polymer structure[c]/%	Cyclo-butane polymer structure[c]/%	M_n[d]/Da × 10^{-4}	D[d]	Yield/%
1	Poly(**1a**)	CQ/EDMAB	25	78	22	0.8	1.5	62[e]
2	Poly(**2a**)	CQ/EDMAB	25	93	7	1.3	1.9	64[e]
3	Poly(**1a**)	AIBN	70	59	41	8.9	1.8	57[f]
4		DTBP	120	50	50	4.4	1.9	51[f]
5	Poly(**2a**)	AIBN	70	86	14	1.3	2.5	56[f]
6		DTBP	120	75	25	1.1	2.9	58[f]
7	Poly(**1a**)	CQ/EDMAB	25	86	14	5.5	2.9	24[g]
8		CQ/EDMAB/DPIHFP	25	80	20	2.0	2.1	77[g]
9	Poly(**2a**)	CQ/EDMAB	25	95	5	1.0	2.7	15[g]
10		CQ/EDMAB/DPIHFP	25	86	14	1.7	2.2	63[g]

[a] Monomer: 0.3 g. [b] 1 mol% CQ; 2 mol% EDMAB, 2 mol% DPIHFP. [c] Estimated by ^{1}H NMR in CDCl₃, polymer structure illustrated in Schemes 7 and 9 and Fig. 5 and S13–S17.† [d] Estimated by GPC; bimodal distribution of poly(**2a**). [e] Yield in 12 h. [f] Yield in 8 h. [g] Yield in 1 h.
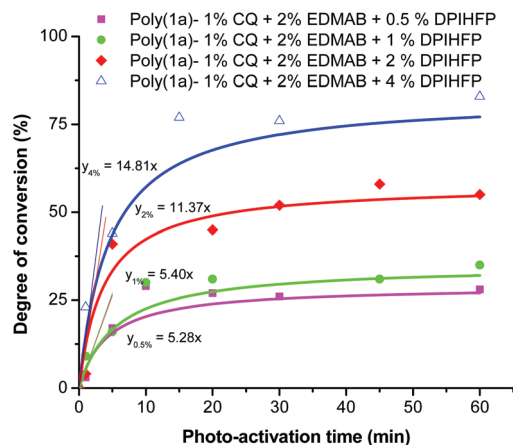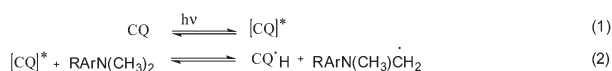
Fig. 4 Degree of conversion for the photo-polymerization of monomer **1a** with different concentrations of DPIHFP as the ternary initiator.


Scheme 4 Schematic simplified reaction scheme of CQ/EDMAB initiation.

The photo-initiator system CQ/EDMAB is frequently used for dentistry applications as the absorption maximum of CQ is around 470 nm, beyond the UV wavelength. Camphorquinone as a 1,2-diketone compound forms a reactive excited species (CQ*) during light absorption (eqn (1)).[23] These excited species interact with the EDMAB to form an exciplex, and within CQ* abstracts, with a hydrogen atom from the tertiary amine to give a ketyl radical and the α-amino-alkyl radicals (eqn (2)), which initiate the polymerization at the carbon double bond of the monomer (eqn (6)). Meanwhile the ketyl radical mainly dimerizes or disproportionates.[23] The simplified reaction mechanism of CQ/EDMAB is shown in Scheme 4.[23,24]

The reaction mechanism using a ternary photo-initiator system is more complex to understand, as Ogliari *et al.* and other authors have already described.[17,24] For consideration of our mechanism only the radical pathway has been described, as we observed that polymerization propagation was based only on radical species and not the cationic one (description further below). The amine radical generated from the exciplex state between CQ* and EDMAB (eqn (2)) could react with DPIHFP, irreversibly cleaving the C–I bond to generate a reactive phenyl radical (eqn (3)). This phenyl radical can either react with the remaining amine, abstracting a proton and generating a new amine free radical or simply start propagation (eqn (7)). It is also reported elsewhere that an exciplex between CQ* and DPIFHP is initially formed, which reacts further with the EDMAB, giving a radical amine species that initiates the polymerization and regenerates the DPIFHP (eqn (5)).[18] Beyond that the DPIFHP can be reduced by an electron transfer within the exciplex with CQ* to a diphenyliodine free radical, which is unstable and decomposes into a phenyliodine
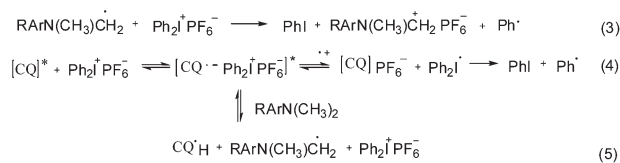
Scheme 5 Simplified scheme of the radical initiation reaction of the ternary photo-initiator system using DPIHFP as the onium salt.
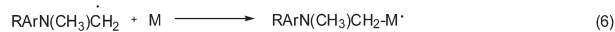
Scheme 6 Schematic propagation initiations during photo polymerization.

and again to a phenyl free radical (eqn (4)).[17,24] Photo-polymerization experiments with monomer **1a** were performed in the presence of the radical inhibitor, hydroquinone. It was observed that the polymerization of **1a** was completely inhibited in ternary systems (CQ/EDMAB/DPIHFP). This result indicated that the polymerization mechanism of the ternary initiation system (CQ/EDMAB/DPIHFP) was the only free radical mechanism for VCP polymerization, and not concurrently radical and cationic, as known for ternary initiator systems with onium salts (Schemes 5 and 6).[12]

Altogether, it can be concluded that the addition of the iodonium salt DPIHFP opens further pathways capable of generating radicals, whereby compared to the binary initiator system CQ/EDMAB, on the one hand the relative efficiency of the radical initiation is increased, while on the other hand an increased concentration of initiating radicals results simply by using DPIHFP as the ternary initiator.

3.1 Structure of the polymer

It has been described by Sanda *et al.* that a 1,5-type ring-opened polymer unit is primarily formed in the thermal polymerization of 1,1-disubstituted 2-vinylcyclopropanes with minor amounts of cyclobutane containing units (Scheme 7).[3,19]

The polymer structure of poly(**1a**) made by photo-polymerization was examined in detail by ^{1}H-NMR (Fig. 5), and compared with the structures formed using thermal radical polymerization. According to the reported literature a broad signal between 1.5 and 2.5 ppm in ^{1}H NMR is caused by the formation of a cyclobutane containing unit (**1a**$_{II}$) for thermally polymerized samples.[3] This broad signal was not as clearly observed in poly(**1a**) obtained from photo-polymerization, as in the polymers obtained during thermal polymerization with AIBN or DTBP (Fig. 5).
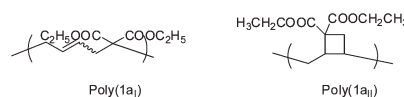
Scheme 7 Expected polymer structures for monomer (**1a**).
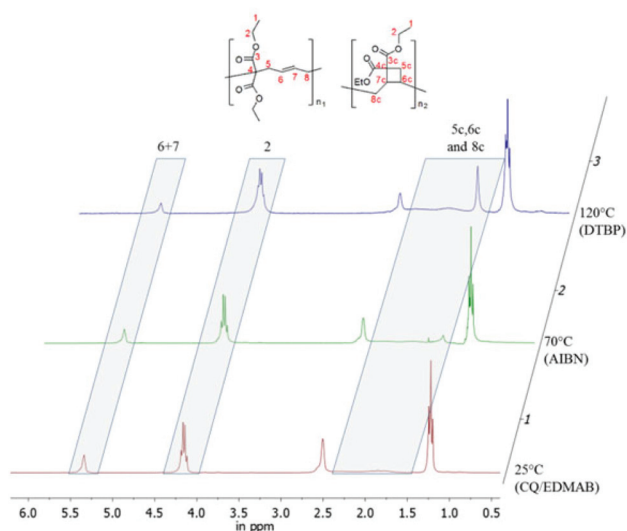
Fig. 5 Overlay of three ^{1}H-NMRs of poly(**1a**) (solvent CDCl[3], 300 MHz), polymerized by (1) 1 mol% CQ and 2 mol% EDMAB at 25 °C; (2) 1 mol% AIBN at 70 °C; (3) 1 mol% DTBP at 120 °C.

Nevertheless we could not observe a 92% percent ring opened structure (**1a**[I]) for poly(**1a**), polymerized thermally with AIBN at 70 °C,[3] rather we calculated only 59% of the ring opened structure (Table 1). To determine the amount of the ring opened structure for poly(**1a**) and poly(**2a**) equally, the ^{1}H-NMR integral values of the ethyl ester protons (proton signal 2 within Fig. 4) have been normalized to a value of four, as these exhibit an analogous chemical shift for the ring opened and the cyclobutane units. Thereby the total proton values were congruent to the expected one (16 protons for poly(**1a**) and 18 for poly(**2a**)). The ratio of the olefinic protons (signal 6 + 7 in Fig. 5) to the expected protons (for 100% ring opening) distinguished directly the amount of the ring opened structure.

A reduced amount of cyclobutane-containing units **1a**[II] (Scheme 7) for poly(**1a**) and **2a**[III] and **2a**[IV] (Scheme 9) for poly(**2a**) could be observed, as the temperature for the polymerization was reduced to room temperature for photopolymerizations (Table 1). This is in accordance with the literature[3,4] in which the cyclobutane units increased as the polymerization temperature of the thermal polymerization increased.

From ^{1}H-NMR data, it was also evident that the presence of the onium salt DPIHFP and the reaction time did influence the ring opened structure of the polymers **1a** and **2a** (Table 1). Naturally with rising reaction time, viscosity as well as conversion increased leading to increased amounts of cyclobutane-containing units (entries 1 and 7; Table 1). The increase in cyclobutane units with increasing conversion, as a matter of increasing melt viscosity was also evident on addition of the onium salt DPIHFP (*i.e.* use of the ternary initiator system). Using a binary initiator system, the conversions of **1a** and **2a** were very low and unlike ternary initiator systems with DPIHFP, no glass-like state was observed by equivalent exposure times (please compare entries 7 with 8 and 9 with 10

in Table 1) giving less cyclobutane units. The cyclobutane units were formed by the addition of a newly formed radical during propagation to the double bond in the polymer main chain. It is a competitive reaction with the reaction of the ring-opened propagating radical with a new VCP monomer. With an increase in reaction viscosity and prolonged reaction time the addition of the ring-opened radical at the double bond of the same molecule giving cyclobutane units became more probable.

The effect of temperature on volume shrinkage has been mentioned in various publications,[25–27] usually as a matter of thermal curing effects and changes in the rates of polymerization. Nevertheless, by comparison of the volume shrinkages of poly(**1a**) and (**2a**) polymerized thermally by AIBN at 70 °C[3] with the volume shrinkages of those polymerized by photopolymerization, the effect of volume shrinkage could not be only explained by curing effects or changed rates in polymerization. Rather the polymerization behavior, and much more, the percentage of the ring opened polymer structure (Table 1) are relevant to the volume shrinkage, as the volume shrinkage of poly(**1a**) and poly(**2a**) is disproportionately reduced, compared to the effect of curing and changed rates of polymerizations for methylmethacrylate (MMA) and styrene (St) (Fig. 6).

As mentioned in the Experimental part the synthesized monomer **2a**, other than mentioned by Sanda *et al.*,[19] consists of a constitution isomer of around 80 : 20 (Fig. 1). Nevertheless, it was exhibited that the existence of the constitution isomer did not influence the polymer structure overall, as head and tail conjunctions results in nearly the same polymer structure (Scheme 8).

In addition the main structure of poly(**2a**) was concluded to be chiefly composed of 1,5-ring-opened units, with lower ratios of cyclobutane units compared to polymer **1a** (Table 1). Sanda *et al.*[19] examined intensely through ^{13}C-NMR spectroscopy, that within the polymer structure of poly(**2a**) a *cis* and a *trans* unit were assigned, which could be confirmed, as we observed within two-dimensional NOESY measurements
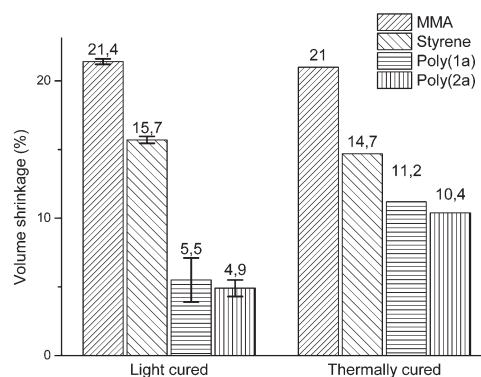

Fig. 6 Comparison of volume shrinkages of MMA, St, poly(**1a**) and poly-(**2a**) dependent on the polymerization method (light curing at 25 °C with CQ and EDMAB as initiators; thermal curing with AIBN at 70 °C.[3,19] The volume shrinkage of the light cured samples was adjusted to complete monomer conversion, by determination of the polymerization yield by ^{1}H-NMR (Fig. S18†).
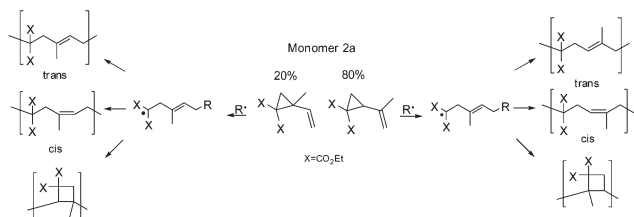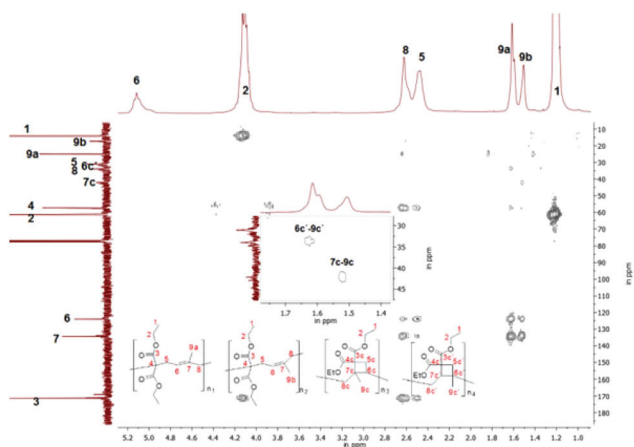
Scheme 8 Schematic description of the expected polymer structures for monomer (**2a**).
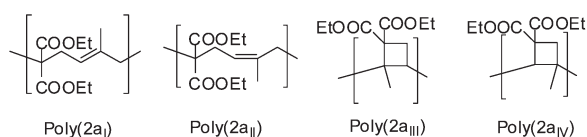
Scheme 9 Proved polymer structures for monomer (**2a**).

Fig. 7 2D-HMBC NMR of poly(**2a**) (solvent CDCl$_3$, 300 MHz), (polymerization conditions: 1 mol% CQ; 2 mol% EDMAB, 2 mol% DPIHFP), inclusive an expansion to verify the correlation between 6c′–9c′ and 7c-9c.

only cross peaks for 9a-5 (*trans* isomer), whereas the *cis* configuration was proved by the absence of an NOE correlation (Fig. S17†).

Furthermore the constitution isomer of the methyl substituted monomer (**2a**) seemed to be promising for the verification of the cyclobutane unit, as this unit could not be explicitly proved currently, because of the difficult characterization, as only a broad signal for poly(**1a**) was observed, that could not be assigned to any protons. Therefore previously the cyclobutane unit was assumed with the missing of the olefinic protons and the respectively higher volume shrinkage.[3,19] In contrast to the polymer structure of poly(**1a**) for poly(**2a**) further cross correlations for the methyl group (9a–c′) of the substructure **2a**$_{III}$ and **2a**$_{IV}$ (Scheme 9) should be verifiable during a two-dimensional HMBC measurement (Fig. 7). Thus a unique interpretation of the polymer signals has been iterated by ^{1}H-, ^{13}C-, HSQC-, NOESY (all shown in the ESI†), HMBC-NMR (Fig. 7) measurements.

Indeed from the HMBC spectra for poly(**2a**) further correlation signals of the methyl groups were present that are assumed to belong to the correlation signals of 6c′–9c′ (**2a**$_{III}$) and 7c-9c (**2a**$_{IV}$) of the cyclobutane unit, whereby to our knowledge, this cyclobutane unit has been detected directly for 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane for the first time.

4.   Conclusions

In summary, 1,1-disubstituted 2-vinylcyclopropanes undergo radical photopolymerization with a reduced formation of cyclobutane units and increased 1,5-type ring-opening compared to thermally polymerized specimens. The reduced amount of cyclobutane units was proportional to the volume shrinkage. In addition, we varied the photopolymerization conditions to observe the impact on reaction kinetics. The addition of the onium salt DPIHFP as a ternary initiator to the radical initiator system drastically reduced the curing time for bulk polymerizations. This makes VCPs attractive as a monomer component in low shrinking dental adhesives or composites.

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