Polymerization of Cyclic Monomers. VII. Synthesis and Radical Polymerization of 1,3-Bis[(1-alkoxycarbonyl-2vinylcyclopropane-1-yl)carboxy]benzenes

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ABSTRACT: 1,3-Bis[(1-alkoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzenes 1 [RO: CH₃O (a), C₂H₅O (b)] were synthesized by the esterification of the corresponding 1-alkoxycarbonyl-2-vinylcyclopropane-1-carboxylic acids with resorcinol. The structure of the new vinylcyclopropanes was confirmed by elemental analysis and infrared (IR), ¹H nuclear magnetic resonance (¹H-NMR), and ¹³C nuclear magnetic resonance (¹³C-NMR) spectroscopy. The radical polymerization of difunctional 2-vinyl-cyclopropanes in bulk with 2,2'-azoisobutyronitrile (AIBN) results in hard, transparent, crosslinked polymers. During the bulk polymerization of the crystalline bis[(1-methoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzene 1a, an expansion in volume of about 1% took place. The radical solution polymerization of 1a resulted in a soluble polymer with pendant 2-vinylcyclopropane groups. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1775–1782, 1999

Key words: radical polymerization; ring-opening polymerization; 2-vinylcyclopropanes; low-shrinking monomers; crosslinking monomers

INTRODUCTION

Cyclic monomers, such as spiro orthocarbonates, spiro orthoesters, or cyclic ketene acetals, may show a near-zero volume shrinkage or, sometimes, expansion in volume during their ringopening polymerization and, therefore, are of interest in the fields of precision castings, dental fillings, or adhesives.¹ In this context, 2-vinylcyclopropanes have also been known as low-shrinking or expanding monomers, which undergo radical ring-opening polymerization to result in polymers bearing mainly a 1,5-ring-opened unit.²⁻⁴ Monomers containing two or three polymerizable vinylcyclopropane moieties and an alkylene or cycloalkylene spacer between them generally dem-

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onstrate a higher rate of polymerization and also a better solvent resistance of the corresponding polymers.⁵ With regard to the mechanical properties of materials, crosslinking monomers with a more rigid arylene spacer between the polymerizable groups should be an advantage.

Previously, we reported about the synthesis and polymerization of asymmetric substituted 1-alkoxycarbonyl-1-phenoxycarbonyl-2-vinylcyclopropanes.⁶ This article describes the synthesis and radical polymerization of 1,3-bis[(1-alkoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzenes 1a/1b. The structure of the new monomers is shown in Figure 1.

EXPERIMENTAL

Materials

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Methylene chloride, methanol, and tetrahydrofuran(e) (THF) were dried over molecular sieves.



Figure 1 1,3-Bis[(1-alkoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzenes 1a/1b.

Resorcinol, 4-dimethylaminopyridine (DMAP), and 1,3-dicyclohexylcarbodiimide (DCC) were used without further purification. 2,2'-Azoisobutyronitrile (AIBN) was purified by recrystallization. Methyl methacrylate (MMA) was washed with a 5.0 wt % NaOH solution, dried over anhydrous sodium sulfate, and distilled from calcium hydride under argon before use. All chemicals were purchased from Fluka (Buchs, Switzerland).

Bisphenol A diglycidyl dimethacrylate (Bis-GMA, Esschem), tri(ethylene glycol) dimethacrylate (TEGDMA, Esschem), the aliphatic urethane dimethacrylate (UDMA, Ivoclar, Liechtenstein) from 2-hydroxyethyl methacrylate and 2,2,4-trimethylhexamethylenediisocyanate, DL-camphorquinone (CC, Rahn, Zurich, Switzerland), and cyanoethylmethylaniline (CEMA, Lonza, Basel, Switzerland) were used without further purification. 1-Methoxycarbonyl-2-vinylcyclopropane-1-carboxylic acid was prepared according to the procedure described previously.⁵ 1-Ethoxycarbonyl-2-vinylcyclopropane-1-carboxylic acid was synthesized in the same way. 1,1-Bis(4-nonylphenoxycarbonyl)-2-vinylcyclopropane (BNPhVCP) was prepared as described in the literature.⁴

The fillers are commercial products, as follows: fumed silica (Degussa, Frankfurt, Germany), YbF₃ (Auer Remy, Hamburg, Germany), an SiO₂-ZrO₂ mixed oxide (Tokoyama Soda), and a barium silicate glass (Schott, Landshut, Germany). Before use, the silica, the mixed oxide, and the glass filler were modified with the silane coupling agent 3-methacryloyloxypropyltrimethoxysilane (Union Carbide). The fillers were silanized by mixing them with 1.0 wt % of water and 5.0 wt % of the silane at room temperature over a period of 2 h and drying the modified fillers at 50°C for 4 days.

Synthesis of 1,3-Bis[(1-alkoxycarbonyl-2vinylcyclopropane-1-yl)carboxy]benzenes 1a and 1b: General Procedure

22.0 g (200 mmol) of resorcinol, 0.5 g (4.1 mmol) of DMAP, and 400 mmol of 1-methoxycarbonyl-2vinylcyclopropane-1-carboxylic acid (for 1a) or 1-ethoxycarbonyl-2-vinylcyclopropane-1-carboxylic acid (for 1b) were dissolved in 200 mL of anhydrous methylene chloride. Then, 82.5 g (0.40 mol) of DCC were added to the stirred solution in portions in a way that the temperature did not surpass 10°C. After stirring overnight at room temperature, the formed precipitate was filtered off. The filtrate was washed with diluted HCl, aqueous NaHCO₃ solution, and brine. After drying over anhydrous sodium sulfate, the solution was evaporated. The crude product was purified by chromatography using a column of silica gel 60 and a mixture of ethyl acetate and hexane (7:3,v/v) as the eluent. The product was obtained by evaporation of the solvent.

1,3-Bis[(1-methoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzene (1a): Yield: 28.2 g (34%) as a white solid [mp (DSC): 72–88°C] after reprecipitation from diethyl ether (solvent)–petroleum ether (precipitating agent). ¹H-NMR (CDCl₃): δ = 1.73–1.90 ppm (m, —CH₂—, 4H); δ = 2.69–2.75 ppm (m, —CH<, 2H); δ = 3.81 ppm (s, —OCH₃, 6H); δ = 5.19–5.55 ppm (m, CH₂=CH—, 6H); 6.96–7.40 ppm (m, H-Arom., 4H). ¹³C-NMR (CDCl₃, 100 MHz): δ = 21.30 ppm (C-4); 32.13 ppm (C-3); 36.82 ppm (C-5); 52.84 ppm (—OCH₃); 115.24 ppm (C-8); 119.12 and 119.33 ppm (C-1/C-10); 129.77 ppm (C-11); 132.47 ppm (C-2); 153.30 ppm (C-9); 167.32 and 167.87 ppm (C-6/C-7). FTIR (KBr): 1755 cm⁻¹ (C=O), 1638 cm⁻¹ (C=C).

ANAL. calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 64.08; H, 5.51.



1,3-Bis[(1-ethoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzene (1b): Yield: 59.3 g (67%) as a high viscous liquid. ¹H-NMR (CDCl₃): δ = 1.29 ppm (t, --CH₃, 6H); 1.72–1.89 ppm (m, --CH₂--, 4H); δ = 2.70–2.72 ppm (m, --CH<, 2H); δ = 4.24 ppm (q, --OCH₂--, 4H); δ = 5.19–5.56 ppm (m, CH₂=-CH--, 6H); 6.94–7.40 ppm (m, H-Arom., 4H). ¹³C-NMR (CDCl₃, 100 MHz): δ = 14.14 ppm (CH₃); 21.35 ppm (C-4), 31.62 ppm (C-3); 35.90 ppm (C-5); 61.81 ppm (--OCH₂--); 115.30 ppm (C-8); 119.19 and 119.29 ppm (C-1/C-10); 129.80 ppm (C-11); 132.83 ppm (C-2); 150.97 ppm (C-9); 165.86 and

167.48 ppm (C-6/C-7). FTIR (KBr): 1731 cm⁻¹ (C=O), 1634 cm⁻¹ (C=C).

Anal. calcd for $C_{22}H_{22}O_8$: C, 65.15; H, 5.88. Found: C, 65.07; H, 6.38.

Polymerization

The radical bulk and solution polymerization was carried out in sealed glass tubes as described previously.⁴ The solution polymerizates obtained were precipitated in cold methanol. The gel particles were suspended in methylene chloride for 48 h, filtered off, and subsequently dried to constant weight under vacuum. The polymerization shrinkage was calculated from the density of the monomers and polymers, which were measured by pycnometry or by the buoyancy method described previously.⁷ The monomer conversion was calculated from the gravimetrically determined yields of the dried polymers. Photopolymerization of monomer mixtures or composites was carried out using CC as the photoinitiator. Flexural strength specimens (2 \times 2 \times 25 mm) were obtained by irradiating the resins with a visible light source (Spectramat, Ivoclar, Schaan, Liechtenstein). The mechanical properties were determined after immersing the specimens in water for 24 h at 37°C. The determination of linear polymerization shrinkage in dependence of irradiation time was performed with an apparatus of the University of Zurich, as described previously.⁸

Poly(1a) (M_n = 62,000 g mol; for sample, see Table II): ¹H-NMR (CDCl₃): δ = 1.64–1.97 ppm (m, —CH₂—_{cyclopr}, 2H); δ = 2.26–3.05 ppm (m, —CH₂—_{chain}/—CH<, 5H); δ = 3.40–4.09 ppm (m, —OCH₃, 6H); δ = 5.19–5.55 ppm (m, CH₂—CH—/—CH—_{chain}, 5H); 6.55–7.39 ppm (m, H-Arom., 4H). ¹³C-NMR (CDCl₃, 100 MHz): δ = 21.26 ppm (C-4); 29.70 ppm (C-17); 32.11 ppm (C-3); 35.82 ppm (C-5); 52.82 ppm (C-12/C-16); 57.78 ppm (C-14); 115.08 ppm (C-8); 119.22 ppm (C-1/C-10); 129.87 and 128.50 ppm (C-11/C-18); 132.51 ppm (C-2); 150.98 ppm (C-9); 167.32, 167.87, 168.85, and 170.47 ppm (C-6/C-7/C-13/C-15):



Composite Preparation

The experimental composites were mixed in either an Exakt roll mill (Exakt Apparatebau, Norderstedt, Germany) in the case of a filler content of 60 wt % or an LPM 2 SP kneading machine (Linden, Marienheide, Germany) for a higher filler loading.

Measurements

¹H-NMR (400 MHz) and ¹³C-NMR spectroscopic measurements (100 MHz) were recorded with a DPX-400 spectrometer (Bruker) using tetramethylsilane (TMS) as the standard and CDCl₃ as a solvent. A Fourier transform infrared FTIR spectrometer 1600 (Perkin-Elmer) was used to record IR spectra. The number-average molecular weight of polymers was determined by gel permeation chromatography (GPC) using THF as the eluent, a ultraviolet (UV) detector Spectra 100, and columns calibrated with poly(styrene) standards. Differential scanning calorimetry (DSC) measurements were performed by using a Perkin–Elmer DSC-7 thermal analyzer. Scanning rates of 10°C min were used. The elemental analvses were performed with an EA 1108 elemental analyzer (Fisons Instr.). Coupling of liquid chromatography with mass spectroscopy was carried out with an API 1 LC/MS system (Perkin-Elmer Sciex). The flexural strength and flexural modulus were determined as usual using a Z 010 universal testing machine (Zwick, Ulm, Germany).⁹

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers

1,3-Bis[(1-alkoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzenes 1a ($R = CH_3$) and 1b ($R = C_2H_5O$) were synthesized by the esterification of the corresponding 1-alkoxycarbonyl-2-vinylcyclopropane-1-carboxylic acid with resorcinol according to Figure 2.

The monomer 1a is a white crystalline substance, whereas 1b is a colorless, highly viscous liquid that is advantageous for practical application. The monomers are stable in the presence of moisture or inorganic dental fillers in contrast to previously investigated 2-methylene-1,3-dioxepanes.¹⁰ In the case of monomer 1b, the investigation of the crude product by LC-MS showed (see Fig. 3) that, besides the main product monomer 1b, the following by-products are formed: approx-



Figure 2 Synthetic scheme for 1,3-bis[(1-alkoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzenes 1a/1b.

imately 5 wt % of the resorcinol monoester (A), approximately 5 wt % of 2-(3-hydroxyphenyl)-1,1dicyclohexylisourea (B), and approximately 10 wt % of a monomer (C), which contains three 2-vinylcyclopropyl groups. Furthermore, the 1-(1-ethoxycarbonyl-2-vinylcyclopropane-1-oyl)urea (D) and the 1-ethoxycarbonyl-2-vinylcyclopropane-1-carboxylic anhydride (F) are also formed in a quantity of less than about 1.0 wt %. In the meantime, the new compounds (A), (C), and (F) were synthesized.¹¹

The characterization of the new vinylcyclopropanes was carried out by ¹H-NMR, ¹³C-NMR, IR spectroscopy, and elemental analysis. The spectra data are in agreement with the expected structure. For example, the formation of the 2-vinylcy-clopropane unit is supported by the presence of multiplets assignable to CH of the cyclopropane ring at $\delta = 2.69-2.75$ ppm or to the vinyl group at $\delta = 5.19-5.55$ ppm in the ¹H-NMR spectrum of 1a (Fig. 4). Furthermore, the ¹H-NMR signal of the aromatic hydrogen is an expected multiplet at 6.96–7.40 ppm. The ¹³C-NMR spectrum also confirms the presence of two different signals at 167.32 and 167.87 ppm, assignable to CO of the ester bonds.

Polymer and Composite Synthesis and Characterization

The new monomers 1a and 1b were homopolymerized in bulk and solution, respectively, in the presence of AIBN. The results show (Table I) that the radical bulk polymerization of the liquid 2-vinylcyclopropane 1b is accompanied by a change in volume (Δv) of -3.9 vol %, whereas in the case of the crystalline monomer 1a, an expansion in volume of 0.9 vol % takes place. The expansion in volume of monomer 1a is probably caused by the transition of the denser structure of the crystalline monomer in a less-compressed structure of the amorphous polymer formed. The commonly used crosslinking methacrylates, such as bisphenol A diglycidyl dimethacrylate (Bis-GMA) or tri(ethylene glycol) dimethacrylate (TEGDMA) show a polymerization shrinkage of approximately 6.1 (Bis-GMA) or 14.2 vol % (TEGDMA). Therefore, it can be concluded that the vinylcyclopropanes 1a and 1b are compounds with a significantly lower polymerization shrinkage in comparison to the crosslinking methacrylates.

For both 2-vinylcyclopropanes, the bulk polymerization resulted in highly transparent solid products, which are insoluble in common organic solvents, which confirms the crosslinking properties of the synthesized monomers. This is a further advantage of the multifunctional 2-vinylcyclopropanes, which generally leads to materials with improved mechanical properties and improved solvent resistance in comparison to the monofunctional 2-vinylcyclopropanes.

In order to obtain more information about the structure of polymers formed, the polymerization of the monomers 1a and 1b was also carried out in a diluted solution of chlorobenzene. The results show (Table II, Fig. 5) that monomer 1a is more reactive in comparison to monomer 1b, which was not expected because of the similar structure of the two monomers. With a monomer concentration of only 0.30 mol L, the solution polymerization results in soluble polymers; whereas in the



Figure 3 By-products of the synthesis of 1,3-bis[(1ethoxycarbonyl-2-vinylcyclopropane-1-yl)carboxy]benzene 1b identified by liquid chromatography-mass spectroscopy.



Figure 4 ¹H-NMR spectrum of 1,3-bis[(1-methoxycarbonyl-2-vinylcyclopropane-1-yl)-carboxy]benzene 1a.

case of a higher monomer concentration, gels were formed. Therefore, a high amount of crosslinked polymers are formed within a few hours.

In case of the soluble polymers, only one 2-vinylcyclopropyl group of each difunctional monomer molecule should participate in the polymer chain formation. From the literature, it is known¹² that the radical polymerization of 1,1-

Table IBulk Polymerization of Monomers 1aand 1b and of Crosslinking Methacrylates

Monomer	$\Delta V \; (\text{Vol } \%)^{\mathrm{b}}$
1a ^a 1b TEGDMA UDMA	$^{+1.0}_{-3.8}$ 14.2 6.1

 $^{\rm a}$ Initiator, AIBN (2.5 mol %); temperature, 65°C; polymerization time, 15 h.

^b Change of volume estimated from density of the monomers and polymers. disubstituted 2-vinylcyclopropanes is mainly a ring-opening polymerization under the formation of 1,5-ring-opened polymer units. Furthermore, the formation of polymers containing cyclobutane units was discussed. The ¹H-NMR spectrum of the soluble poly(1a), which is formed as the result of the solution polymerization, shows (Fig. 6) the signals that are assignable both to 1,5-ring-

Table II	Solution Poly	merization o	f Monomers
1a and 1b	o in Chloroben	zene ^a	

Monomer	Time (h)	Polymer Yield (Wt %)	M_n (g mol) ^b
1a	1.0	57.8	62000
1a	5.0	83.5	c
1b	1.0	14.5	30000
1b	5.0	65.9	c

 $^{\rm a}$ [Monomer], 0.30 mol L; initiator, AIBN, 2.5 mol %; polymerization temperature, 65°C; polymerization time, 15 h.

^b Number-average molecular weight, evaluated by GPC.

° Not determined.

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Figure 5 Polymerization of monomer 1a (0.30 mol L) in the presence of AIBN (2.5 mol %) in chlorobenzene at 65° C.

opened polymer units and the laterally bonded 2-vinylcyclopropyl groups, for example, the broad signal at 5.1–5.9 based on (—CH==CH) protons of the main chain and (CH₂==CH--) protons of the lateral vinylcyclopropyl group. Above all, the ¹³C-NMR spectrum confirms the structure of the soluble poly(1a), for example, the four peaks in the carbonyl region at 167.32, 167.87, 168.85, and 170.47 ppm or, in comparison to the ¹³C-NMR spectrum of the monomer, the new signal at 29.70 ppm, which is assignable to the —CH₂— group of the 1,5-ring-opened monomer unit. Therefore, the



Figure 7 Scheme of the mechanism of the radical polymerization for the monomers 1a/1b in solution.

formation of soluble polymers can be characterized according to Figure 7.

The radical copolymerization of 1a with MMA was carried out in chlorobenzene solution (Table III). The results show that the polymer yield and the molecular weight of the polymers formed decrease with an increasing content of monomer 1a. That means that the difunctional monomer 1a is



Figure 6 ¹H-NMR spectrum of poly(1a) formed in solution.

[1a] (mol L)	[MMA] (mol L)	Polymer Yield (Wt %)	M_n (g mol) ^b
0	1.00	11.5	33,200
0.20	0.80	10.3	20,900
0.50	0.50	3.6	17,400

Table III	Copolymerization of Monomer	1a
with MM	A in Chlorobenzene ^a	

 $^{\rm a}$ [AIBN], 0.02 mol L; polymerization temperature, 65°C; polymerization time, 30 min.

^b Number-average molecular weight, evaluated by GPC.

less reactive than MMA. This is also confirmed by the fact that the content of monomer 1a in the copolymer, formed on the basis of the equimolar monomer mixture, is only 18 mol %.

In that case, the 2-vinylcyclopropanes are able to copolymerize with methacrylates. The potential of crosslinking 2-vinylcyclopropanes as a matrix monomer of particulate composites was studied, starting from mixtures of commonly used methacrylates with 2-vinylcyclopropanes. As can be seen in Table IV, the flexural strength and the flexural modulus of a particulate composite based on the monofunctional 2-vinylcyclopropane BPh-VCP are significantly lower than those of composites based on the crosslinking monomers 1a/1b. Furthermore, the results for 1b show inferior mechanical properties in comparison to 1a. This is caused by the higher flexibility of the ethoxycarbonyl derivative 1b compared to the methoxycarbonyl derivative 1a. This is also confirmed by the fact that the glass transition temperature T_G of soluble poly(1a) of $(T_G = 72^{\circ}C)$ is higher than that of soluble poly(1b) ($T_G = 65^{\circ}$ C).

Table VMechanical Properties of HighlyFilled Composites^a Containing 2-Vinylcyclopropane Monomer

Monomer	Flexural Strength (MPa)	Flexural Modulus (GPa)
BNPhVCP	92.0 103 7	7.65
1b	109.1	9.10

^a Composition of the composites: 52.4 wt % of milled barium silicate glass, 12.8 wt % of YbF₃, 13.7 wt % of SiO₂-ZrO₂ mixed oxide, 1.0 wt % of silica, 4.0 wt % of 2-vinylcyclopropane, 7.5 wt % of UDMA, 8.4 wt % of Bis-GMA, and 0.2 wt % photoinitiator (CC-CEMA); the mechanical properties were measured after storage of the test specimen in water for 24 h.

The mechanical properties of a particulate composite can be further improved by increasing the filler content. As can be seen in Table V, crosslinking 2-vinylcyclopropane containing particulate composites with a filler content of approximately 80 wt % show a flexural strength of approximately 104 to 109 MPa and flexural moduli of approximately 9 GPa, which is acceptable for dental applications. Moreover, monomers 1a and 1b are used to substitute TEGDMA in dental composites, which results in both a decrease in the linear shrinkage and a change of the shrinkage kinetics of the light-curing adhesives or composites. Consequently, a reduced amount of marginal failure and microleakage in in vitro experiments were found.8

CONCLUSION

1,3-Bis[(1-alkoxycarbonyl-2-vinylcyclopropane-1-yl)carboxyl]benzenes 1 [RO: CH₃O (a), C₂H₅O (b)]

Monomer	Storage Conditions ^b	Flexural Strength (MPa)	Flexural Modulus (GPa)
BNPhVCP	24 h, Dry	56.3	1.71
	24-h Water storage	55.0	1.49
	7-d Water storage	51.1	1.59
1a	24 h, Dry	79.0	3.84
	24-h Water storage	88.5	4.40
	7-d Water storage	92.0	4.60
1b	24 h, dry	65.8	2.94
	24-h Water storage	79.6	3.44
	7-d Water storage	67.3	2.99

Table IV Mechanical Properties of 2-Vinylcyclopropane Monomer Containing Composites^a

^a Composition of the composites: 41.4 wt % of silica, 18.6 wt % of YbF₃, 7.8 wt % of 2-vinylcyclopropane, 31.8 wt % of UDMA, and 0.4 wt % of photoinitiator (CC–CEMA).

^b Storage conditions of the test specimen after the mechanical properties were measured.

can be synthesized by the esterification of the corresponding 1-alkoxycarbonyl-2-vinylcyclopropane-1-carboxylic acids with resorcinol. The radical bulk polymerization of the difunctional 2-vinylcyclopropanes results in hard transparent highly crosslinked polymers, and the polymerization of the crosslinking 2-vinylcyclopropanes is accompanied by only a small change of volume. Furthermore, the 2-vinylcyclopropanes are stable in the presence of moisture and commonly used inorganic fillers and, therefore, are useful as a monomer component of low-shrinking materials.

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