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Polymerization of Cyclic Monomers. 5 [1] Synthesis and Radical Polymerization of 4-Methylene-3,5-dioxabicyclo[5.1.0]octane

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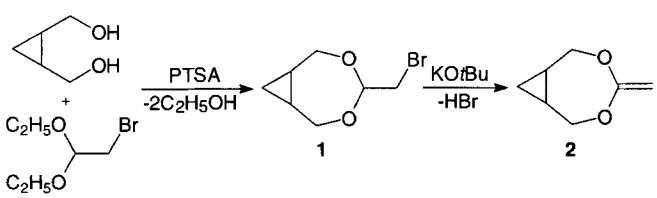
Cyclic monomers, such as spiro orthocarbonates or spiro orthoesters, can show a near zero volume shrinkage or sometimes expansion in volume during their ring-opening polymerization. Therefore, they are of interest in the fields of precision casting, dental fillings, or adhesives [2]. 2-Methylene-1,3-dioxepane derivatives are known as monomers which polymerize radically with almost quantitative ring-opening in the presence of di-*tert*-butyl peroxide (DTBP) at 120 °C and with radical photoinitiators at room temperature [3–5], respectively. In this context, we showed [5] that bicyclic 2-methylene-1,3-dioxepanes primarily undergo a radical ring-opening polymerization, while their cationic photopolymerization is mainly a vinyl polymerization. Previously, we reported about the synthesis and polymerization of unsaturated spiro orthocarbonates [6] and vinylcyclopropanes [1,7].

The ring-opening behaviour of cyclic monomers can be influenced by fusing them with a strained ring. Therefore, the present paper describes the synthesis of 4-methylene-3,5-dioxabicyclo[5.1.0]octane (**2**) and the radical and cationic polymerization of **2** and of 2-methylene-1,3-dioxepane (MDE) as a model compound.

The monomer **2** was prepared by dehydrobromination of bromomethyl dioxepane **1** with potassium *tert*-butoxide with 63% yield. Compound **1** can be obtained by acetalization of (*Z*)-1,2-bis(hydroxymethyl)cyclopropane with bromoacetaldehyde diethyl acetal in the presence of *p*-toluenesulfonic acid (PTSA) with 77% yield. The synthesized bicyclic monomer **2** is a colourless liquid compound which is only stable under exclusion of moisture or acid compounds.



The characterization of the new bicyclic monomer **2** was carried out by ^1H NMR, ^{13}C NMR, IR spectroscopy and elemental analyses. The formation of the cyclopropane ring is supported by the presence of the peaks assignable to CH_2 or CH of the cyclopropane ring at $\delta = 0.67–1.47$ ppm in the ^1H NMR spectrum. The chemical shift of the singulett of the methylene protons is at 3.51 ppm, whereas the signal arising from the carbon atom 4 is at about $\delta = 165.27$ ppm.

The radical polymerization of **2** and MDE was carried out in the presence of D*t*BPO at 120 °C. In case of MDE, highly viscous polymerizates with number-average molecular weights of 7700 or 9150 g/mol were obtained. Contrary to this, the radical bulk polymerization of **2** yielded crosslinked polymers (Tab. 1).

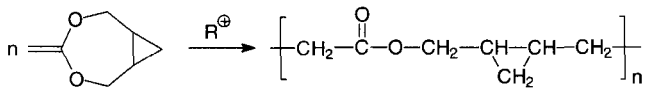
Tab. 1 Bulk polymerization of 4-Methylen-3,5-dioxabicyclo[5.1.0]octane (**2**) and MDE in the presence of D*t*BPO at 120 °C, polymerization time 16 h

Monomer	[D*t*BPO] (mol-%)	Conversion (%)	M_n (g/mol)
MDE	2.5	83.9	7700
MDE	1.0	76.2	9150
2	2.5	54.0	insoluble product
2	1.0	42.3	insoluble product

The spectroscopic characterization of the obtained polymers clearly shows that during the radical polymerization of the bicyclic monomers **2** and of MDE, respectively, opening of the ketene acetal ring has taken place. For example, the IR spectra of both poly[**2**] and poly[MDE] show a strong C=O absorption at 1734 cm^{-1}. Moreover, the ^{13}C NMR specta of poly[MDE] also confirms the polyester formation. The radical formation of crosslinked poly (**2**) is probably caused by a chain transfer reaction under participation of the two reactive

tertiary C–H in monomer **2** and the ring-opened polymer, respectively.

The cyclic ketene acetals **2** and MDE were also polymerized in the presence of the cationic photoinitiator Cyracure UVI 6479 (1.0 wt.-%) which is a mixture of two triarylsulfonium hexafluoroantimonates and yields both cations and radicals under UV light exposure. In case of MDE, the monomer conversion after 20 minutes was nearly quantitative, resulting in an insoluble product. **2** yielded a highly viscous product with a monomer conversion of about 71.0% and a number-average molecular weight of 3 100 g/mol. 2-Methylene-1,3-dioxepanes are very prone to an electrophilic attack of initiating cations within a short time. In contrast to this, the monomer conversion of 2-methylene-1,3-dioxepanes under free-radical conditions is very low within a polymerization time shorter than 1 h. Therefore, it can be assumed that in case of the used photoinitiator and polymerization conditions, the cationic polymerization mechanism is dominating. In the IR spectrum of poly[MDE] obtained by cationic polymerization, the C=O absorption at 1740 cm^{-1} is only weak in contrary to the strong C=O absorption of poly(**2**) at about 1731 cm^{-1}. The ^{13}C NMR spectrum of poly(**2**) also shows the signal of the carbonyl group at 169.45 ppm, which is typical for the ring-opening polymerization mechanism. Unfortunately, the IR spectrum of the poly[MDE] does not offer an indication of a cationic crosslinking mechanism.



2 poly(**2**)

From these results, it can be concluded that the bicyclic monomer **2** shows mainly a ring-opening polymerization under both radical and cationic conditions. MDE shows a polymerization behaviour similar to the recently [5] investigated bicyclic 2-methylene-1,3-dioxepanes having both a 1,3-dioxepane-ring and a 1,3-dioxolane-ring. That means, in the presence of a free-radical initiator, a ring-opening polymerization of these monomers occurred, whereas in the presence of a cationic initiator primarily vinyl polymerization took place. In contrast to this, the dioxepane-ring in **2** is probably more strained resulting in a ring-opening under both radical and cationic conditions.

Experimental

^1H NMR measurements were recorded on an EM 390 (Perkin-Elmer, 90 MHz), AC 300F (Bruker, 300 MHz) or DPX-400 spectrometer (Bruker, 400 MHz) using tetramethylsilane (TMS) as the standard. ^{13}C NMR spectroscopic measurements were performed with a AC 300F spectrometer (Bruker, 75 MHz) using $CDCl_3$ or dimethylsulfoxide-d_6 as a solvent. An FT-IR spectrometer 1600 (Perkin-Elmer) was used to record IR spectra.

(Z)-1,2-Bis(hydroxymethyl)cyclopropane was prepared according to the literature [9]. Ethanol and tetrahydrofuran (THF) were dried over molecular sieves. Bromoacetaldehyde diethyl acetal was purified by distillation. Unless stated otherwise, all other reagents were purchased from Fluka and used without further purification. MDE (Wacker) was distilled before use. The photoinitiator, a mixture of 4-(diphenylsulfonio)phenylphenylsulfide-hexafluoroantimonate and bis[4-(diphenylsulfonio)-phenyl]sulfide-bis-(hexafluoroantimonate) (Cyracure UVI 6974, Union Carbide), was used without further purification.

(E/Z)-4-Bromomethyl-3,5-dioxabicyclo[5.1.0]octane (**1**)

In a 250 mL two-necked flask with a Vigreux-column (20 cm), distillation head and magnetic stirrer 0.83 g (4.36 mmol) PTSA was added to a mixture of 41.7 g (0.41 mol) (Z)-1,2-bis(hydroxymethyl)cyclopropane and 84.7 g (0.43 mol) bromoacetaldehyde diethyl acetal. After evacuation to 22 mbar, the stirred reaction mixture was heated to 50 °C under evaporation of ethanol for 60 min. Then, the temperature of the reaction mixture was increased continuously for 1 h to the boiling point of the product (112-113 °C/22 mbar). Subsequently, the product was distilled, resulting in a colourless liquid with 77% yield.

$C_7H_{11}BrO_2$ Calcd.: C 40.60 H 5.35
(207.07) Found.: C 40.48 H 5.48.

– ^1H NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.46–1.52 (m;4H,CH/CH_2-cyclopropyl), 3.21–3.42 (m;2H,CH_2Br), 3.85–4.30 (m; 4H,CH_2O,) and 4.55–4.61 (m, 1H, CHCH$_2$Br). – ^{13}C NMR (75 MHz; $CDCl_3$, δ (ppm)): 16.23, 16.68, 18.10 (C-cyclopropyl), 32.45 (CH_2Br), 68.56 and 74.24 (CH_2O), 106.37 and 108.36 (CHCH$_2$Br). – IR (film, cm^{-1}): 623 (w), 698 (m), 830 (w), 910 (w), 1001 (s), 1029 (s), 1055 (s), 1118 (s), 1151 (s), 1206 (s), 1284 (s), 1367 (s), 1424 (m), 1463 (m), 2862 (s), 2947 (s) and 3004 (m).

4-Methylene-3,5-dioxabicyclo[5.1.0]octane (**2**)

A solution of 30.0 g (0.14 mol) (E/Z)-4-bromomethyl-3,5-dioxabicyclo[5.1.0]octane (**1**) in 90 mL THF was added to a suspension of 18.5 g (0.16 mol) potassium *tert*-butoxide in 200 mL THF. The mixture was heated to reflux with stirring for 8 h, filtered off and after addition of 5.0 mg hydroquinone monomethylether, the filtrate was evaporated in vacuo. The crude product was purified by vacuum distillation, resulting in a colourless liquid with 63% yield.

$C_7H_{10}O_2$ Calcd.: C 66.65 H 7.99
(126.16) Found.: C 66.62 H 7.75.

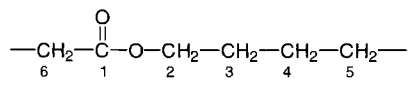
– ^1H NMR (90 MHz, $CDCl_3$, δ(ppm)): 0.67–1.03 (m;2H,CH_2-cyclopropyl); 1.18–1.47 (br; 2H,CH-cyclopropyl), 3.51 (s; 2H,CH_2=), 3.92 (dd; 2H,CH_2) and 4.27 (dd; 2H,CH_2). – ^{13}C NMR (75 MHz, $CDCl_3$, δ(ppm)): 10.88 and 15.70 (C-cyclopropyl), 69.79 and 70.16 (CH_2O/CH_2=) and 165.27 (CH_2=C<). – IR (film, cm^{-1}): 658 (m), 716 (w), 791 (s), 891 (s), 1035 (s,sh), 1158 (m), 1214 (s), 1288 (s), 1379 (s,sh), 1462 (m), 1594 (m), 1672 (s), 2885 (m), 2946 (m), 3005 (m) and 3073 (w).

Polymerization

Radical polymerization was carried out in bulk in sealed glass tubes as previously described [10]. The obtained polymerizates were dissolved or suspended in THF. The polymer solutions or suspensions were precipitated in cold *n*-hexane and

then reprecipitated with THF/*n*-hexane. For photoinitiated polymerization, a mixture of about 1 g monomer and 0.8 wt.% cationic photoinitiator was photopolymerized under ambient conditions using a Spectramat™ lamp (Ivoclar), which produces intensive light in a wavelength range from 320 to 500 nm. The polymerizates were dissolved or suspended in 10 mL THF and precipitated in 100 mL n-hexane. All polymers were dried under reduced pressure to a constant weight.

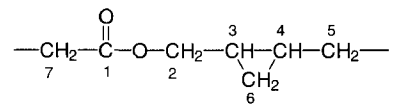
Poly(MDE) (D*t*BPO, M_n = 9150 g/mol): – IR (KBr, cm^{-1}): 739 (w), 1065 (m), 1102 (m), 1165 (s), 1359 (m), 1461 (m), 1734 (s) and 2954 (m). – ^1H NMR (400 MHz, $CDCl_3$, δ (ppm)): 0.92–0.95 (m; CH_3 end-groups), 1.35–1.43 (m; 2H,C(5)H_2), 1.59–1.69 (m; 4H, –C(3)H_2–C(4)H_2–), 2.29–2.45 (m; 2H, –CH_2–CO–), 4.05–4.23 (m; 4H, –CO–O–CH_2–). – ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm)): 13.71 (CH_3 end-groups), 24.60, 25.52, 28.45 and 34.11 (C2/C3/C4/C5), 64.12 (C6) and 173.51 (C1).



Poly(**2**) (*D*tBPO): – IR (KBr, cm^{-1}): 944 (m), 994 (m), 1067 (m), 1164 (s), 1256 (s), 1383 (m), 1459 (m), 1648 (m), 1734 (s) and 2959 (m).

Poly(MDE) (Cyracure UVI 6479): – IR (KBr, cm^{-1}): 596 (w), 929 (m), 961 (m), 1023 (s), 1056 (s), 1159 (s), 1231 (m), 1362 (m), 1439 (m), 1740 (w) and 2938 (m).

Poly(**2**) (Cyracure UVI 6479, M_n = 3100 g/mol): – IR (KBr, cm^{-1}): 826 (w), 929 (m), 961 (m), 1023 (s), 1047 (s), 1114 (s), 1180 (s), 1231 (m), 1363 (m), 1428 (m), 1731 (s) and 2944 (m). – ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm): 3,02 (C7), 14,11 and 17,56 (C3/C4), 31,55 and 34,49 (C2/C5), 62,92 (C7) and 169,45 (C1).



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