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Synthesis and Photoinitiated Cationic Polymerization of 2-Methylene-7-phenyl-1,4,6,9-tetraoxaspiro[4.4]nonane

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ABSTRACT: Synthesis of the asymmetrically substituted 2-methylene-7-phenyl-1,4,6,9-tetraoxaspiro-[4.4]nonane monomer in four steps and its polymerization are described. The spiromonomer is liquid at room temperature. Photoinitiated cationic polymerization of 2-methylene-7-phenyl-1,4,6,9-tetraoxaspiro-[4.4]nonane at ambient temperature in bulk was investigated, using a cationic photoinitiator system based on (η^5-2,4-cyclopentadiene-1-yl)[1,2,3,4,5,6-η](1-(methylethyl)benzene)iron(I) hexafluorophosphate (Irgacure 261). Upon irradiation, within 10 min quantitative double ring-opening polymerization to a structurally well-defined poly(alkylene−carbonate−ketone) with molecular weight average M_w of 27.000 (GPC) occurred. No elimination, vinylidene polymerization, or single ring-opening polymerization was detected, as commonly observed in the case of free-radical initiation of similar spiroorthocarbonates, spiroorthoesters, or methylenedioxolanes were detected. Despite quantitative double ring opening, no volume expansion occurred during polymerization. A volume shrinkage of 4.1% was found. General structural prerequisites for expanding and pseudoexpanding monomer systems are discussed.

INTRODUCTION

The development of monomer systems that show low shrinkage or even expansion during polymerization is intriguing with respect to applications as matrix resins for dental restoration, high-strength composites, adhesives, coatings, precision castings, and sealant materials.[1,2]

Volume shrinkage during polymerization is due to the reduction of van der Waals distances between monomer molecules to covalent bond lengths.[2] The total value of the shrinkage during polymerization is determined by the following factors: (i) degree of polymerization (number of addition steps), (ii) size of the monomers (large molecules show lower shrinkage than small monomers), (iii) state of monomer and resulting polymer, i.e., isotropic liquid, crystalline, or amorphous solid, and (iv) type of polymerization (condensation, polyaddition, ring opening, double ring opening).[2]

Various strategies have been employed to reduce shrinkage during polymerization: (i) use of high molecular weight resins or monomers with large substituents, (ii) ring-opening polymerization (ROP), or (iii) double ring-opening polymerization (DROP). In the latter case, for every newly formed bond in the polymers, covalent bonds in the monomers have to be broken. Quantitative ROP or DROP is desirable because side reactions, such as elimination or vinyl polymerization, cause increased shrinkage.

Since the first reports on double ring-opening polymerization in 1972,[3] several bicyclic monomers, such as spiroorthoesters (SOE) and spiroorthocarbonates (SOC) have been developed that show volume expansion during polymerization. However, most of these compounds are crystalline under ambient conditions or polymerize only under partial double ring opening,[1−4] which severely limits their practical applicability. Therefore, such monomers are commonly polymerized in the melt at elevated temperature, where their actual density is lower than in the crystalline state, which is of no practical use. Moreover, low molecular weight fragments, formed during photocure, can act as plasticizers to reduce volume shrinkage. The phase transition accounts for the apparent volume expansion. An important objective is to develop liquid matrix resins that undergo quantitative DROP upon irradiation.

This paper explores the volume reduction during quantitative DROP, which may be viewed as clean isomerization polymerization. We considered liquid monomer systems with spirocyclic structures that are polymerizable under exclusive double ring opening crucial for this purpose. Liquid spirocyclic monomers have been described;[5−7] however, either no DROP took place,[5] the volume change was not determined,[6] or expansion was postulated but not experimentally verified.[7] Based on the recently described, fast cationic photopolymerization of 2-phenyl-4-methylene-1,3-dioxolanes in bulk,[8] we report the synthesis and photoinitiated cationic polymerization of the asymmetrically substituted 2-methylene-7-phenyl-1,4,6,9-tetraoxaspiro-[4.4]nonane (**4**, Figure 1). The (η^5-2,4-cyclopentadiene-1-yl)[1,2,3,4,5,6-η][1-(methylethyl)benzene]iron(I)-hexafluorophosphate (**5**) was employed as cationic photoinitiator (Figure 1). This compound leads to formation of the cationic initiator species **5a** ([INI]$^+$ in Scheme 2) after extrusion of cumene (Figure 1).

EXPERIMENTAL SECTION

Materials. Diphenyl carbonate (Fluka), phosphorus pentachloride (Fluka), 3-chloro-1,2-propanediol (Fluka), phenyl-1,2-ethanediol (Fluka), triethylamine (Fluka), and dichloromethane (Riedel-De-Haen) were obtained in p.a. quality and used without further purification. Tetrahydrofuran (THF; Roth) was purified by distillation from sodium. For precipitation of the polymers, methanol (technical grade) was used. The cationic photoinitiator (η^5-2,4-cyclopentadiene-1-yl)[1,2,3,4,5,6-η][(1-methylethyl)benzene]iron(I) hexafluorophosphate (**5**) was obtained from Ciba-Geigy (trade name Irgacure 261). Irgacure 261 can be employed under ambient conditions and exhibits good stability upon storage for prolonged periods.

Methods. ^{1}H- and ^{13}C-NMR spectra of monomer and polymer were recorded on a Bruker AMR 300 spectrometer using TMS as internal standard in CDCl$_3$ at ambient temperature. IR spectra were obtained with a Perkin-Elmer 1330 IR spectrometer. GC spectra were recorded with a GC 6000 Vega Series 2 controlled by an ICU 600 (Carlo Erba Instru-

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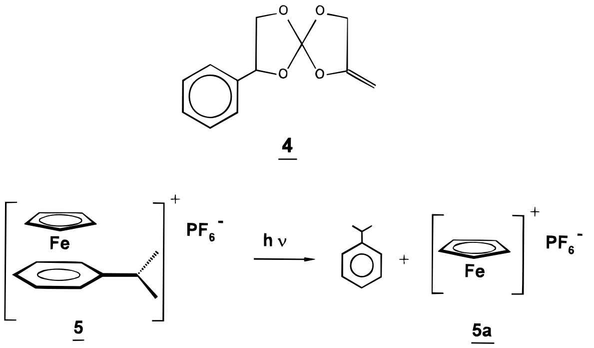


Figure 1. Monomer **4** and cationic photoinitiator **5**.

ments) using the following heating rates: start 60 °C, 20 °C/min to 100 °C, (holding 1 min), 20 °C/min to 300 °C (holding 5 min). For GPC, a combination of 10^5, 10^3, and 100 nm PL columns (Polymer Laboratories) was employed; $CHCl_3$ was used as solvent. All data are referenced to narrow polystyrene standards. The monomer density was determined by means of a pycnometer, and the density of the polymer was determined from buoyancy in distilled water. The volume shrinkage was calculated from $(D_{pol} - D_{mon})/D_{pol}$.

Synthesis of the Monomer. An overview of the synthesis of **4** is shown in Scheme 1. Unless noted otherwise, all manipulations were carried out under Ar.

Preparation of Dichlorodiphenoxymethane (1). A mixture of 228.4 g (1.07 mol) of diphenyl carbonate and 233 g (1.12 mol) of phosphorus pentachloride was stirred at 200 °C for 9 h. The phosphorus oxychloride formed was removed by continuous distillation. The separation was completed under reduced pressure. The resulting reaction mixture was distilled in vacuum: bp 130 °C (0.1 mbar) (lit.[9] bp 183–185 °C (12 mmHg); yield 246.6 g (86%, lit.[9] yield 80%). **1** is very sensitive to hydrolytic decomposition to form dihydroxydiphenoxymethane and diphenyl carbonate and therefore has to be handled carefully: ^{1}H NMR ($CDCl_3$): δ 7.37, 7.25 ppm (10H). ^{13}C NMR ($CDCl_3$): δ 152.17 (O_2CCl_2), 150.98 (arom C1), 122.28 (arom C2), 129.26 (arom C3), 126.3 (arom C4) ppm.

Preparation of 4-(Chloromethyl)-2,2-diphenoxy-1,3-dioxolane (2). To a solution of 101.5 g (0.92 mol) of 3-chloro-1,2-propanediol and 256 mL (185.8 g, 1.84 mol) of triethylamine in 200 mL of dichloromethane was added dropwise a solution of **1** (246.6 g, 0.92 mol) in 300 mL of dichloromethane at room temperature with stirring. After completion of the addition, the reaction mixture was stirred for 6 h at room temperature. The suspension was washed twice with 100 mL of water and the aqueous layer extracted with 50 mL of dichloromethane. The organic phases were dried over anhydrous potassium carbonate. After removal of the solvent, the residue was purified by vacuum distillation: bp 175 °C (0.1 mbar) [lit.[9] bp 171–173 °C (0.35 mmHg)); yield 194.7 g (69%, lit.[9] yield 64%). ^{1}H NMR ($CDCl_3$): δ 3.18, 3.43 ($OCHCH_2Cl$), 4.45 (m, 1H), 3.93 (m, 1H), 4.2 (m, 1H), 7.15, 7.29 ppm (2s, 10H, arom H). ^{13}C NMR ($CDCl_3$): δ 43.0 (CH_2Cl), 75.85 ($OCHCH_2Cl$), 68.28 ($OCHRCH_2O$), 127.4 (spiro-C), 152.21, 151.97 (arom C1, arom C1′), 121.27, 121.91 (arom C2/C6, arom C2′/C6′), 129.01, 129.11 (arom C3/C5, arom C3′/C5′), 124.68, 125 ppm (arom C4, arom C4′). IR (neat): 2900, 2960, 3030, 3060 (ν_{H-C-H}), 1450, 1483, 1585 ($\nu_{arom\ C=C}$), 1085 (ν_{C-O}), 688, 750 cm^{-1} (arom monosubst). Anal. Calcd for $C_{16}H_{15}O_4Cl$: C, 62.65; H, 4.93; Cl, 11.56. Found: C, 62.32; H, 4.90; Cl, 11.32. GC: 98.5% (rt 12.48).

Preparation of 2-(Chloromethyl)-7-phenyl-1,4,6,9-tetraoxaspiro[4.4]nonane (3). To a solution of **2** (100 g, 0.33 mol) in 250 mL of dichloromethane, a solution of 45 g (0.33 mol) of phenylethanediol and 0.5 g (2.6 mmol) of *p*-toluenesulfonic acid monohydrate in 100 mL of dichloromethane was added dropwise at room temperature. After addition was completed, the reaction mixture was immediately washed with 1 M sodium hydroxide (200 mL × 9). The organic layer was dried over anhydrous potassium carbonate. After solvent evaporation, the residue was purified by vacuum distillation: bp 124 °C (0.1 mbar), yield 44.2 g (52.2%). ^{1}H NMR ($CDCl_3$): δ 3.62 (m, 2H, $OCHCH_2Cl$), 3.91 (m, 1H), 4.04, 4.12 (m, 2 × 0.5H), 4.29 (m, 1H), 4.41 (m, 1H), 4.53 (m, 1H), 5.28 (benzyl-H) 7.32 ppm (s, 5H, arom H). ^{13}C NMR ($CDCl_3$): δ 43.07 (CH_2Cl), 75.12 ($OCHCH_2Cl$), 67.41 ($OCHRCH_2O$), 78.28 ($OCHPhCH_2$), 71.51 ($CHPhCH_2O$) 134.98 (spiro-C), 126.15, 128.51, 136.89, 137.11 ppm (arom C). IR (neat): 2900, 2960, 3030, 3060 (ν_{H-C-H}), 1455, 1495, 1600 ($\nu_{arom\ C=C}$), 1070 (ν_{C-O}), 695, 760 cm^{-1} (arom monosubst). Anal. Calcd for $C_{12}H_{13}O_4Cl$: C, 56.15; H, 5.10; Cl, 13.81. Found: C, 56.58; H, 5.27; Cl, 13.78. GC: 85.3% (rt 11.14).

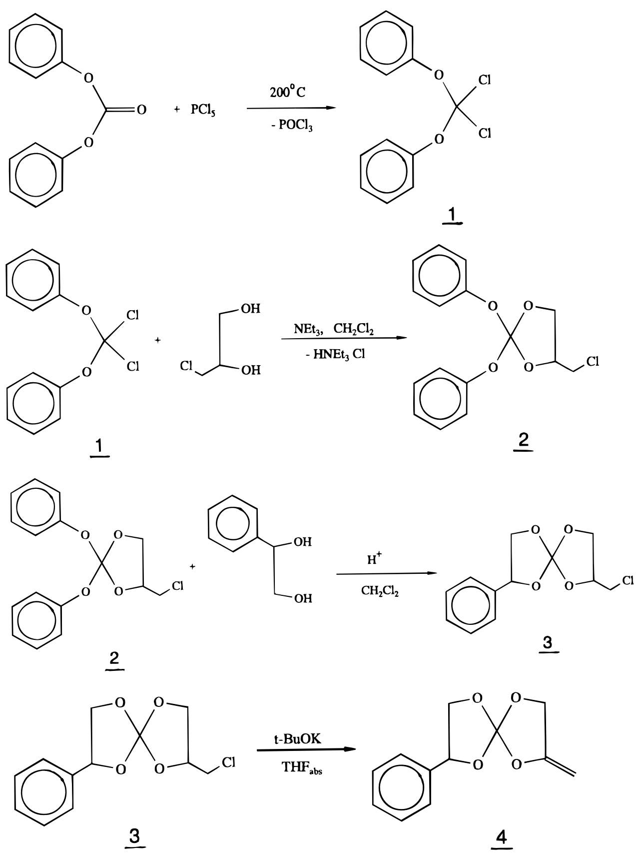
Preparation of 2-Methylene-7-phenyl-1,4,6,9-tetraoxaspiro[4.4]nonane (4). A 20-g (0.08 mol) sample of **3** was added dropwise to a stirred solution of 17.5 g (0.156 mol) of potassium *tert*-butoxide in 150 mL of THF(abs) at a temperature of −4 °C. After completion of the addition, the reaction mixture was allowed to warm to room temperature and then stirred at 60 °C for 3 h. Subsequently, after cooling to room temperature, water was added until a clear solution (separated in two phases) was obtained. The organic layer was separated and the solvent removed under reduced pressure. The residue washed with 7% aqueous $NaHCO_3$ solution (30 mL × 3). The aqueous phase was extracted with diethyl ether, and the organic phases were dried over anhydrous potassium carbonate. After removal of the solvent, the residue was purified by vacuum distillation: bp 97 °C (0.1 mbar); yield 10.5 g (59.7%). ^{1}H NMR ($CDCl_3$): δ 3.9–4.01 (m, 2H, $PhCHCH_2$), 4.39–4.5 (m, 2H, $CH_2{=}CCH_2$), 4.60, 4.68 (m, 2H, $CH_2{=}C$), 5.26–5.35 (q, 1H, benzyl-H), 7.26–7.43 ppm (m, 5H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 80.30 ($=CH_2$), 66.7 ($OCH_2C=$), 78.69 ($OCHPhCH_2$), 71.74 ($PhCHCH_2O$), 135.16 (spiro-C), 152.51 ($OC{=}CH_2$), 126.03 (arom C2), 126.12 (arom C4), 128.48 (arom C3), 136.58, 136.78 ppm (arom C1). IR (neat): 2880–3150 (ν_{H-C-H}), 1680 ($\nu_{C=C}$) 1455, 1495, 1600 ($\nu_{arom\ C=C}$), 1070 (ν_{C-O}), 695, 755 cm^{-1} (arom monosubst). Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.67; H, 5.60. GC: 97.2% (rt 9.51 and 9.56, two diastereomers).

Photoinitiated Cationic Polymerization of 4. Cationic initiator **5** (0.2 wt %) was mixed with 1 g of the monomer **4** and deposited on a glass surface as thin film. This mixture was photopolymerized under ambient conditions using a Dentacolor XS (Kulzer) lamp (250 mW/cm^2 flux), which produces intense light in a spectral range from 320 to 520 nm. The exposure was continued until the reaction mixture had completely solidified, which commonly occurred after 10 min. The obtained clear, brittle solid was dissolved in 5 mL of $CHCl_3$ and added dropwise into 200 mL of stirred methanol at 0°C. A white precipitate was obtained, which was dried under reduced pressure: yield 0.85 g (85%). ^{1}H NMR ($CDCl_3$): δ 1.75–2.18 (m, 1H) and 2.6–3.0 (m, 1H, $COCH_2CHPh$), 3.5–3.7 (s, 0.8 H) and 4.0–4.7 (m, 4.2 H, $PhCHCH_2O$, $COCH_2O$ and benzyl-H), 7.25 ppm (m, 5H, arom H). ^{13}C NMR ($CDCl_3$): δ 39.56 (benzyl-C), 41.0 ($PhCHCH_2CO$), 70.79 (OCH_2CO), 71.08 ($PhCHCH_2O$), 127.72, 127.47, 128.85 (arom CH), 139.65 (arom C) 154.42 (OCOO), 201.44 ppm (C=O). IR (neat): 2920, 2950, 3020, 3050 (ν_{H-C-H}), 1455, 1495, 1600 ($\nu_{arom\ C=C}$), 695, 755 (arom monosubst), 1730 ($\nu_{C=O}$), 1750 cm^{-1} ($\nu_{C=O}$ in OCOO). T_g: 42 °C. M_w: 27 000. M_n: 7500. M_w/M_n: 2.61 (PS standard). Volume shrinkage: 4.1% (based on the density of the monomer).

RESULTS AND DISCUSSION

The synthesis of the spirocyclic monomer **4** was achieved via four steps as shown in Scheme 1. Stansbury mentioned the use of monomer **4** for radical polymerization;[17] however, no synthetic details or shrinkage values were given in the report. The first two reaction steps of our synthetic sequence were carried out according to a procedure of Endo and co-workers.[9] Diphenyl carbonate was dichlorinated to afford dichlorodiphenoxymethane (**1**), using phosphorus pentachloride under continuous removal of phosphorus oxychloride. **1** was reacted with 3-chloro-1,2-propanediol to 2,2-diphenoxy-4-(chloromethyl)-1,3-dioxolane (**2**), which was

Scheme 1. Synthesis of Monomer 4



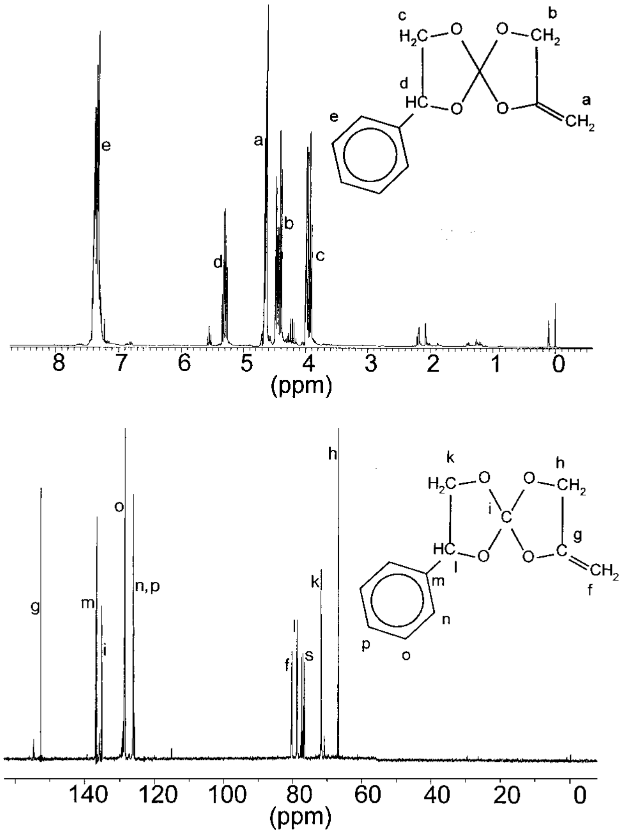


Figure 2. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of monomer **4**.

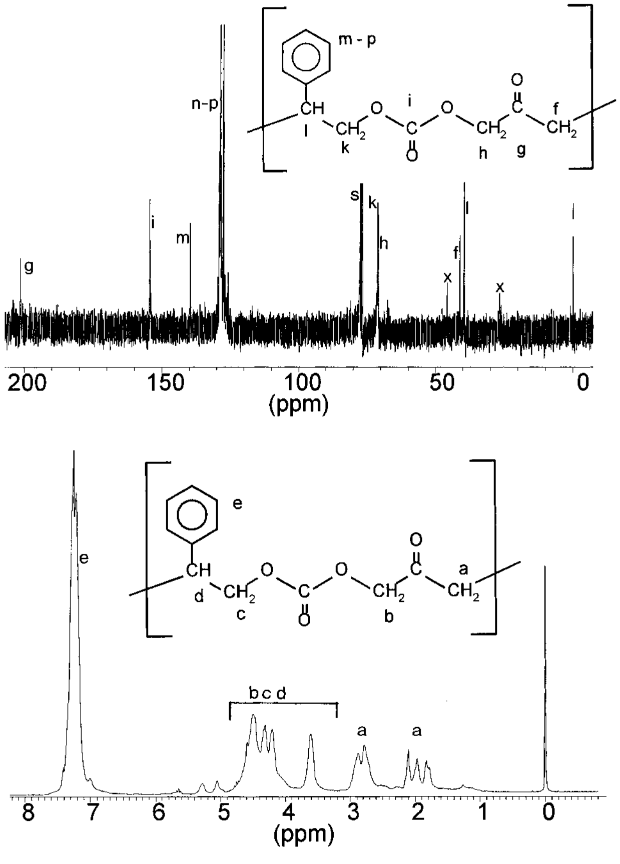
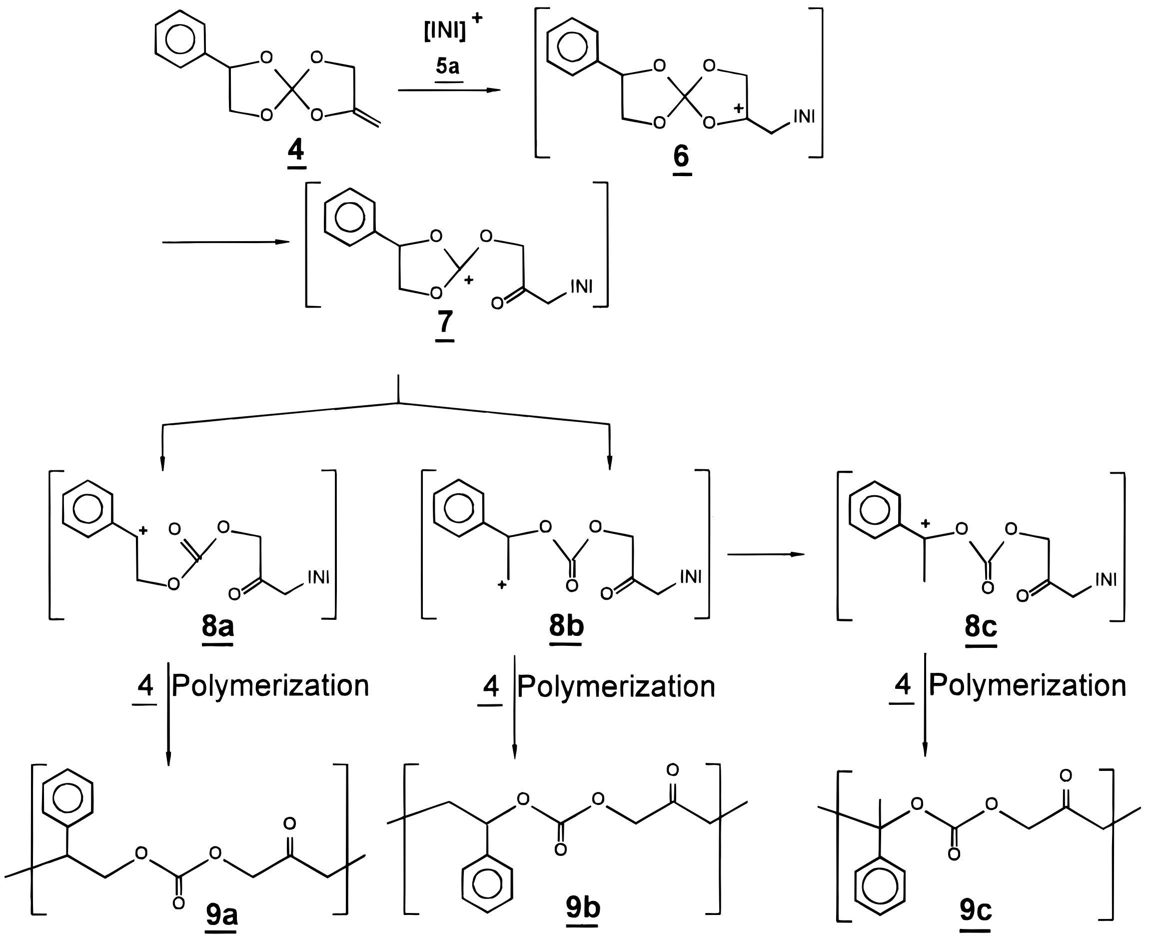


Figure 3. ^{13}C-NMR (top) and ^{1}H-NMR (botttom) spectra of polymer **9** obtained after cationic photopolymerization of **4**.

obtained as a highly viscous liquid. 1-Phenyl-1,2-ethanediol was reacted with **2** to prepare 2-(chloromethyl)-7-phenyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**3**). This reaction was the most difficult step of the four-step procedure, as the catalyst *p*-toluenesulfonic acid monohydrate not only catalyzes the condensation but also promotes ring opening of the diphenoxydioxolane. This side reaction, however, is slow, which allows one to obtain **3** in moderate yields (52%) after short reaction times. Therefore, immediately after the addition of a solution of phenylethanediol and *p*-toluenesulfonic acid in dichloromethane to diphenoxymethane in dichloromethane, the reaction was terminated and the mixture extracted with an aqueous NaOH solution. The spiro compound was not sensitive to hydrolysis under basic conditions. Conversion of **3** to the monomer **4** was achieved by dehydrohalogenation with potassium *tert*-butoxide.

Both spiro compounds **3** and **4** were obtained as liquids at ambient temperature and could be distilled in vacuum in spite of the strained double-ring systems. ^{1}H- and ^{13}C-NMR spectra and GC analysis of **4** (Figure 2) evidence that the spiro monomers were obtained in good purity (>97%). In the ^{1}H-NMR spectrum of **4**, besides the aromatic (7.26−7.43 ppm) and the benzylic proton signals there are three other signals which show strong splittings due to the different environments of the protons in the two ring systems of the molecule and the additional chirality of the benzylic carbon, leading to a set of diastereomers. The ^{13}C NMR shows the signals for the spiro carbon (135.13 ppm), the aromatic carbons (126.12, 128.48, 136.58 and 136.78 ppm), and the exocyclic methylene carbon (80.30 ppm). The resonances of the 1,3-dioxolane unit with exocyclic double bond could be assigned in analogy to the structurally similar methylenedioxolane.[8] The other signals could unambiguously be assigned to the carbons of the second ring. The ^{13}C-NMR spectra of **3** (not shown here; see Experimental Section) and **4** only differ in two reso-

Scheme 2. Mechanism of the Cationic Double Ring-Opening Polymerization of Monomer 4



nances. The signal for the chloromethyl carbon (43.07 ppm) is shifted to 80.30 ppm in comparison to the exocyclic methylene carbon. Furthermore, the signal for the carbon adjacent to the chloromethyl group (75.12 ppm) is shifted to 152.51 ppm in **4** (signal g) after the final elimination reaction.

Cationic Photopolymerization of 4. Cationic photopolymerization of **4** was carried out in bulk. After addition of 0.2 wt % of the initiator **5**, the monomer was irradiated in a mold (2−3 mm thickness) under ambient conditions. A commercial xenon lamp with a spectral range between 320 and 520 nm was used. Within 10 min of irradiation, gelation of the reaction mixture was observed. After dissolution in trichloromethane and precipitation in methanol, the polymer was isolated in 85% yield.

The polymer was characterized structurally by ^{1}H- and ^{13}C-NMR spectroscopy (Figure 3). The ^{13}C-NMR spectrum shows signals at 201.44 (carbonyl carbon) and 154.42 ppm (carbonate carbon) that clearly evidence quantitative double ring-opening polymerization and formation of a poly(alkylene−carbonate−ketone). No signals corresponding to unopened rings of the spiro compounds can be detected. Beside these signals, four aromatic carbon resonances, one CH, and three CH_2 units were detected. The resonances at 41.0, 70.79, and 71.08 ppm could be unambiguously assigned to CH_2 units, and the signal at 39.56 ppm was assigned to the CH units (benzylic carbon). The assignments were confirmed by proton-coupled ^{13}C-NMR spectra as well as DEPT experiments.

The ^{1}H-NMR spectrum (Figure 3, bottom) substantiates the findings from ^{13}C-NMR spectroscopy. The integration of the aromatic and the nonaromatic protons in the ^{1}H-NMR spectrum is 5:7, as expected. This gives evidence that no elimination reactions leading to extrusion of small aromatic fragments occurred during polymerization. The splittings of the signals for the protons a, c, and d are due to the asymmetry of d and the resulting different tacticities of segments of the polymer chain.

FT-IR spectra have also been recorded that show the different carbonyl bands for the carbonate (1750 cm^{-1}) and keto groups (1750 cm^{-1}) in the polymer chain, supporting the structural conclusions from NMR.

On the basis of the structure of the polymers, we conclude that quantitative double ring-opening polymerization leading to a well-defined poly(alkylene−carbonate−ketone) has occurred. The initial ring opening, as shown in Scheme 2 proceeds in analogy to the mechanism proposed recently for the cationic polymerization of 2-phenyl-4-methylene-1,3-dioxolane (Ph-MDO),[8] 2-isopropenyl-4-methylene-1,3-dioxolane (IP-MDO),[10,11] or 2-ethenyl-4-methylene-1,3-dioxolane (E-MDO).[12] The mechanism of the first ring opening is comparable to ring opening of these MDOs. The initiator **5** is attacked by the exocyclic double bond of the monomer and the cyclic cation **6** results. The first ring opening results in isomerization to the single ring-opened intermediate **7**. This step is mainly driven by the formation of the energetically favored carbonyl group and formation of a carbocation, which is stabilized by 3 alkoxy groups. Opening of the second ring results again in isomerization to the double ring-opened intermediate **8**, this time by formation of the likewise energetically favoredcarbonate group. Opening of the second ring leads to a stabilized benzyl cation (**8a**) or a methylene cation (**8b**), which is less probable due to structural considerations and thus should easily rearrange to intermediate **8c**. The resulting cations propagate by reaction with monomer. Mechanistic pathway **8c** most probably leads to the signals denoted “x” in the ^{13}C-NMR spectrum shown in Figure 3 (top), due to polymer structure **9c**.

Polymerization leads to the possible repeat units **9a** and **9b** that only differ in the position of the phenyl substituent in the polymer backbone. In **9a** (benzyl cation as intermediate) the phenyl-substituted carbon is located exactly between the carbonyl group and the carbonate group next to two CH_2 units, in **9b** (methylene cation as intermediate), the carbon with the phenyl substituent is situated adjacent to the carbonate group.

Volume Changes during Polymerization. The polymerization was investigated with respect to volume change. The densities of monomer, determined by means of a pycnometer and polymer, determined from buoyancy in distilled water were measured to be 1.210 g/mL for the monomer and 1.262 g/mL for the poly(alkylene–carbonate–ketone). The shrinkage was calculated from $(D_{\mathrm{pol}} - D_{\mathrm{mon}})/D_{\mathrm{pol}}$. This results in a shrinkage of 4.1%, which was verified in a number of polymerization experiments. This value for the volume change is in apparent contradiction to the previously reported compensation of volume shrinkage or even expansion by double ring-opening polymerization proposed by various authors.[1–4,13,14,18]

A number of authors have reported on bicyclic monomers that polymerize with low shrinkage (2–3%) or even expansion, which has been explained by the double ring-opening polymerization. An elegant method for the determination of shrinkage was used by Millich and coworkers who determined densities of monomers and resulting polymer in solution.[13,18] It is obvious that the density of the crystalline state is higher than after melting in the liquid state.[1,2] Therefore, an evaluation of volume changes during polymerization has to take into account the state of the material, i.e., isotropic disorder or crystalline order of the monomer. Thus, the density of an amorphous polymeric product may be appropriately compared only with an isotropic monomer liquid. In current reports on so-called “expanding monomer systems”, mostly crystalline monomers are polymerized to amorphous polymeric products. In this case, the crystalline packing with little free volume leads to low shrinkage or even expansion during polymerization. However, this is mainly due to the variation of the order of the materials, as the polymerization results in an amorphous material with considerably larger free volume. In addition, from a practical point of view it is obvious that crystalline powders are commonly not applicable in this state but generally have to be melted or dissolved in another monomer before polymerization.

At present we are not able to generalize our observations. However, it should be emphasized that despite clean double ring opening no expansion resulted. On the basis of our findings and the results obtained by other investigators, we consider it important to distinguish between “real expansion”, caused by the peculiar features of a polymerization mechanism—such as DROP—and “pseudoexpansion” that is mainly due to a transition of states with different order. In the following, we propose to distinguish between three generally different cases of volume change during polymerization, that are shown schematically in Figure 4.

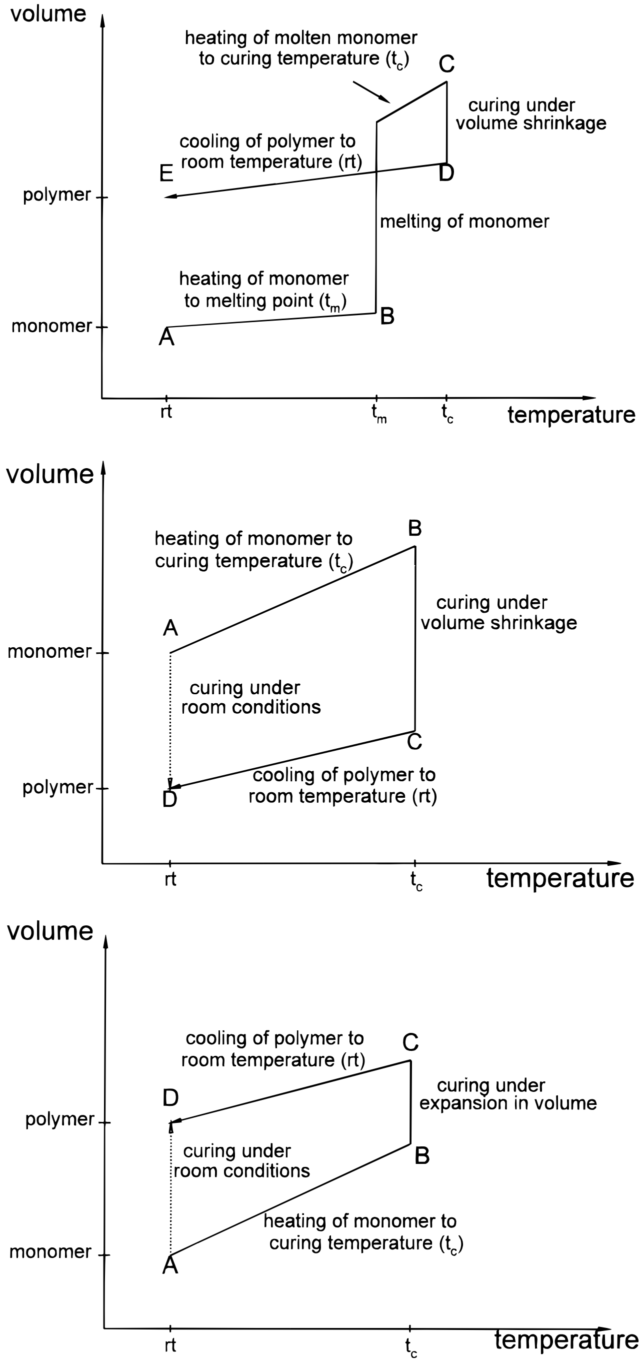


Figure 4. Classification of monomers according to shrinkage behavior during polymerization: crystalline, (pseudoexpanding) (a, top), liquid, (not expanding) (b, middle), and liquid, (real expanding) (c, bottom) monomer systems.

Figure 4a shows the typical behavior observed for systems that are currently described as “expanding monomers”. The crystalline monomer is heated from room temperature to its melting point (A – B) and after melting heated to the reaction temperature (B – C). During polymerization volume shrinkage occurs (C – D), and after the end of polymerization the amorphous polymer is cooled to room temperature (D – E). The expansion in volume is mainly the result of the higher density of the monomer in comparison to polymer density, common for all known crystalline monomers. When crystalline monomers are polymerized in the melt, volume shrinkage occurs.[14–16] Therefore, the system is actually pseudoexpanding.

The behavior of a liquid monomer that exhibits volume shrinkage is shown in Figure 4b. The curing step may be carried out either at ambient conditions (dotted line; A − D) or at elevated temperatures (A − B − C − D). After heating to reaction temperature (A − B), the reaction mixture polymerizes under shrinkage (B − C) and is subsequently cooled to room temperature (C − D). This behavior is generally found for all known liquid monomer-systems.

Figure 4c shows the hypothetical behavior of an expanding liquid monomer that would show true expansion during polymerization. In this system, curing at room temperature (dotted line; A − D) and polymerization at higher temperatures (A − B − C − D) is possible. After heating to the reaction temperature (A − B), the monomer cures under expansion in volume (B − C) and cools to room temperature. Most systems reported in the literature do not show true expansion in this manner.

CONCLUSION

2-Methylene-7-phenyl-1,4,6,9-tetraoxaspiro[4.4]nonane has been prepared in good yields via a four-step synthesis as a liquid spirocyclic monomer with an exocyclic double bond. Photoinitiated cationic polymerization resulted in quantitative double ring opening due to the proved stable intermediate benzylic cation. The product obtained after polymerization is a poly(alkylene−carbonate−ketone). Despite quantitative double ring opening the shrinkage caused by the polymerization of the liquid monomer was 4.1%. Clearly, volume reduction during polymerization has to be discussed with respect to the state of order of monomers and resulting polymer.

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