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Polymerization of 5,5-(Bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one and Copolymerization with 5,5-Dimethyl-1,3-dioxan-2-one

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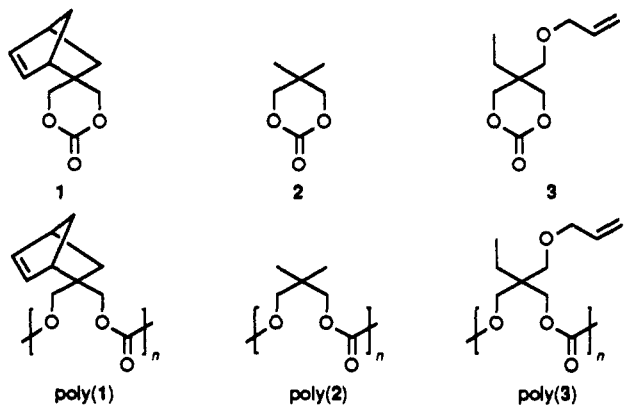
ABSTRACT: The anionic ring-opening polymerization of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (1) gives in high yield poly(1) with a narrow molecular weight distribution (M_w/M_n = 1.1). Exo and endo anions are formed with the same probability. These anions upon further reaction with monomer result in an atactic polymer. The backbiting reaction is severely restricted due to the stiffness of the polymer chain. Deliberate synthesis of a homologous series of cyclic oligomers is induced by transesterification reactions; the active chain end rearranges to endo–exo-linked repeating units before backbiting occurs. The proof for the exo–endo-linked repeat units in the cyclic oligomers as well as the sequence analysis in the polymer is provided by means of ^{13}C NMR spectroscopy. The copolymerization of 1 with 5,5-dimethyl-1,3-dioxan-2-one (2) yields a statistical copolymer. A block copolymer is obtained when the polymerization of the monomers is performed in a stepwise manner. The analysis of the copolymers by ^{13}C NMR gives clear evidence of the kind and proportion of the diads. Thermal analysis of the homo- and copolymers shows that samples obtained by precipitation of the polymer from solution show crystallinity, while samples from the melt or cast as films are amorphous materials.

Introduction

The anionic polymerization of cyclic carbonates such as 5,5-dimethyl-1,3-dioxan-2-one[1] yields a high molecular weight polymer fraction in equilibrium with a low molecular weight fraction of cyclic oligomers. The stiffness of the chain that controls the position of the ring–chain equilibrium as well as the thermal and thermomechanical properties of the polymer depends on the nature of the "spacer" between the carbonate groups in the polymer chain. A comparison of the thermal properties of two polymers investigated in our laboratory, viz., poly(2) and poly(3), both obtained from six-membered cyclic carbonates, may illustrate the situation.[2] Poly(2) is a highly crystalline polymer with T_m = 123.5 °C and T_g = 27 °C while poly(3) is an amorphous polymer with T_g = −29.8 °C.



The present paper reports on the ring-opening polymerization of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (1) and on the copolymerization of 1 with 5,5-dimethyl-1,3-dioxan-2-one (2). The homopolymer was expected to have a rather stiff backbone.

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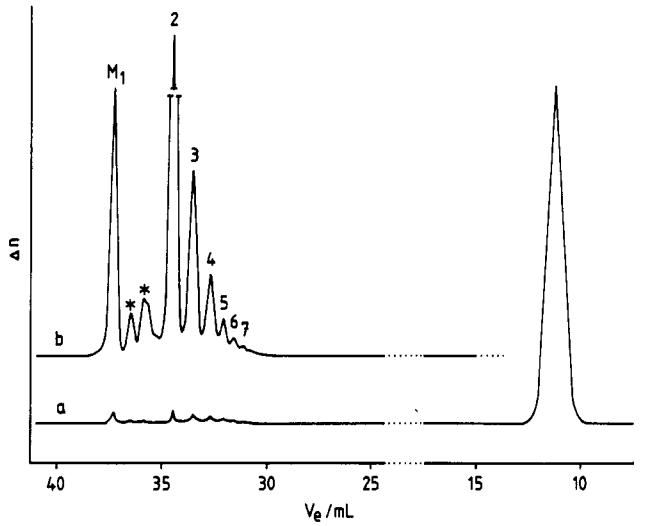


Figure 1. GPC of the product of the polymerization of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (1). (a) Reaction conditions: $[1]_0 = 0.56$ mol/L, $[I]_0 = 2.1$ mmol/L, $T = 0$ °C, $t = 3$ h. (b) Reaction conditions: the active reaction product as shown in (a) was diluted to $[1]_0 = 0.056$ mol/L and equilibrated for 48 h at 25 °C. Δn, difference in index of refraction n. M_1 represents the monomer; * are impurities with strong UV absorption; 2–7 represent the oligomers with degree of polymerization x.

Results and Discussion

Homopolymerization of 5,5-(Bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (1). 5,5-(Bicyclo[2.2.1]-hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (1) was polymerized in toluene solution with *sec*-butyllithium as initiator. The polymerization was initiated at room temperature and conducted at 0 °C. The polymer was isolated and separated from oligomers by precipitation in methanol. The fraction of oligomers is very small (2 wt %), indicating that the backbiting reaction is restricted (see Figure 1). This can be explained by a reduced mobility of the polymer chain. The polymers prepared show molecular weights of 10000–40000 by GPC analysis with polystyrene standards and exhibit a narrow molecular weight distribution ($M_w/M_n = 1.1$).

The conversion of the monomer to the polymer can be followed by means of ^{1}H NMR spectroscopy, monitoring the methylene protons adjacent to the carbonate group. In the monomer, all four protons of the above mentioned methylene groups are magnetically nonequivalent (Figure 2A). In the spectrum of the polymer (Figure 2B), the two methylene groups of the main chain show resonances with different chemical shifts; this is not the case in other unsymmetrically substituted polycarbonates, as for example in poly(3). The two protons at $\delta = 3.92$ ppm are assigned to the methylene group in endo position with respect to the norbornene system, while the protons of the methylene group in exo position are at lower field ($\delta = 4.23$ ppm). The ^{13}C NMR also shows differences between the monomer 1 and the polymer poly(1) (see Figure 3A and 3B). The carbon atoms of the 1,3-dioxan-2-one ring are much more influenced upon ring opening than the carbon atoms of the norbornene system. The C_6 and C=O resonances are shifted downfield from $\delta = 40.1$ to 46.3 ppm and from $\delta = 148.7$ to 155.0 ppm, respectively, C_X and C_N are shifted to higher field from $\delta = 76.4$ to 70.9 ppm and from $\delta = 74.9$ to 70.1 ppm, respectively. On the other hand, the multiplicity of the resonance lines changes. The monomer shows a singlet for the carbonyl carbon atom at $\delta = 148.7$ ppm while poly(1) shows three signals at $\delta = 154.87$, 155.08, and 155.28 ppm with a ratio of the intensities of 1:2:1; the monomer exhibits sharp signals for C_X and C_N, while in the polymer these signals consist of a complex unresolved multiplet. Especially the latter effect indicates that the structure of the polymer is not as uniform as might be expected. Moreover, from the resonances of the carbonyl carbon atom in the polymer, only one conclusion can be drawn: an atactic polymer with Bernoullian statistics is formed. This structure arises from the fact that the monomer can react with the initiator or growing species in two different ways (see Scheme I) with formation of an "endo anion" and an "exo anion". Further reaction of the endo anion with monomer may result again in an endo anion (→ c →) (The arrows suggest the orientation of the norbornene system relative to the carbonate functional group.), or in an exo anion (→ a ←); the exo anion behaves in a corresponding manner, further reaction with monomer leads either to endo anion (← b →) or to exo anion (← d ←). As can be seen from the reaction scheme, three different resonances are expected for the carbonyl carbon atom, namely: (i) an exo–endo carbonate unit as represented in c and d, (ii) an endo–endo carbonate unit represented by a, and (iii) an exo–exo carbonate unit represented by b. If the probability of the formation of each these units is equal, three different structures are expected with a distribution of 1:2:1.

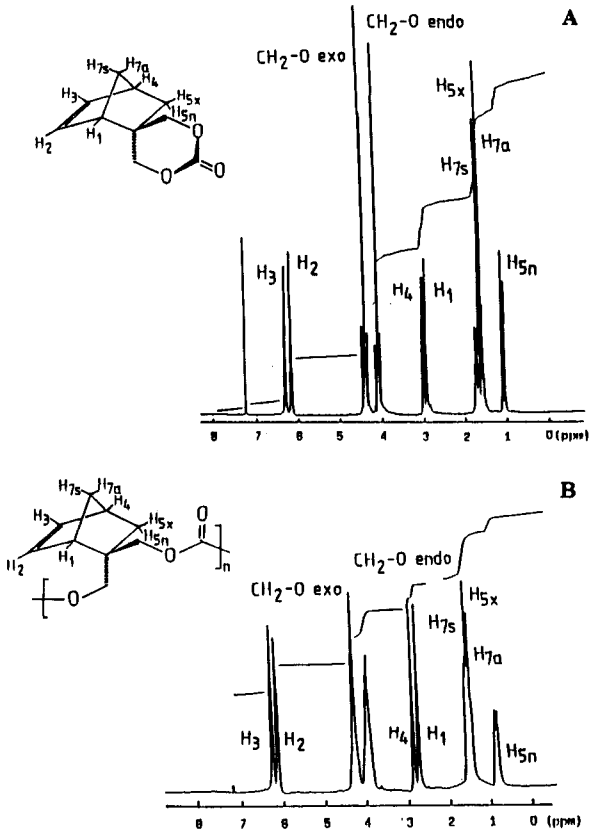


Figure 2. ^{1}H NMR spectra of (A) 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one and (B) poly[5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one].

In order to obtain more insight into the reaction occurring during polymerization, we decided to find reaction conditions under which a high proportion of oligomers is formed. We prepared poly(1) in the usual manner by polymerizing a 10 wt % solution of 1 in toluene, and afterwards we diluted the polymer solution to 1 wt % and analyzed the reaction product after 48 h of stirring at room temperature. Figure 1b shows the GPC after polymerization and after dilution and equilibration of the system. As can be seen, at the beginning of the reaction all the monomer is converted to the polymer (Figure 1a),

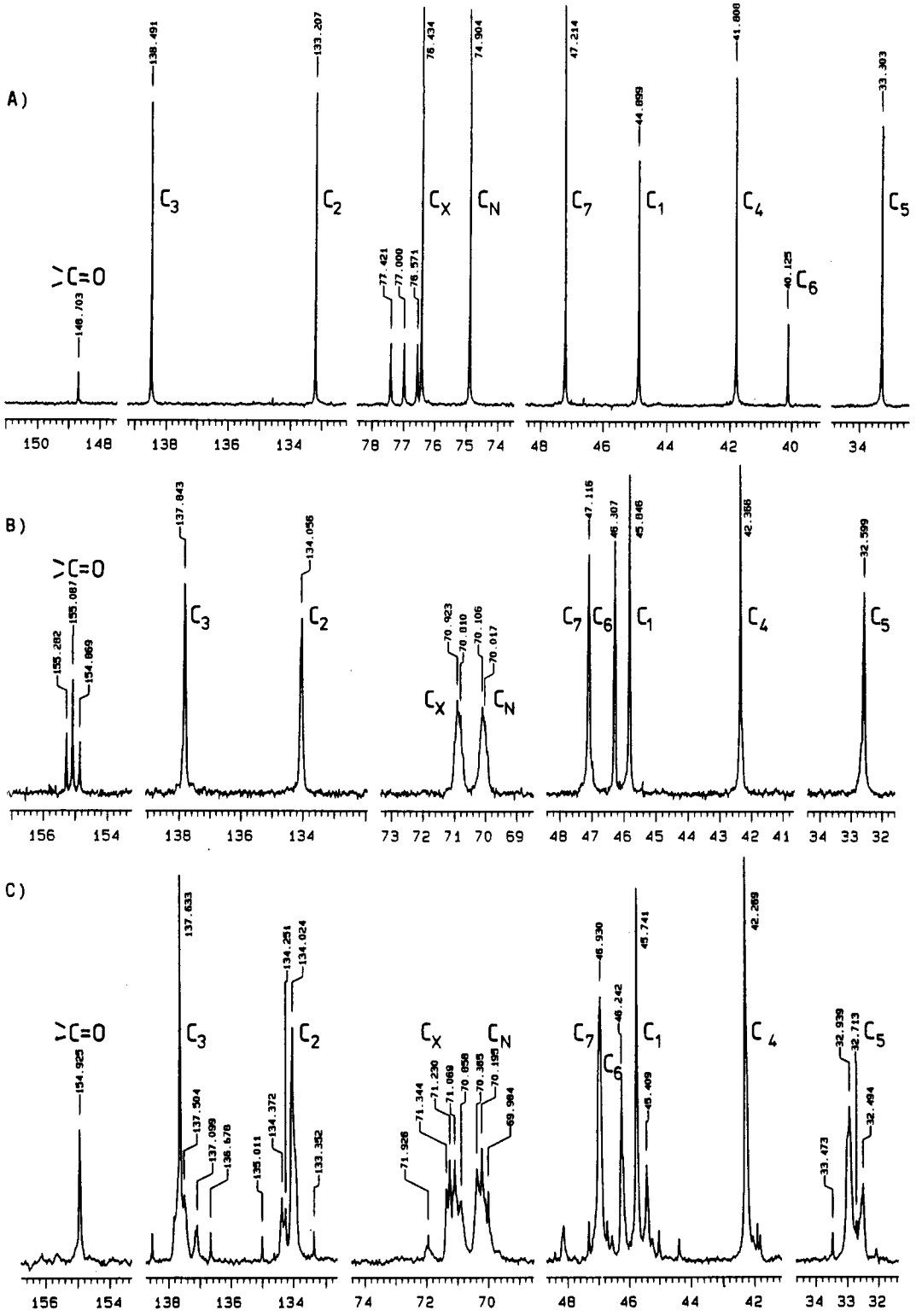
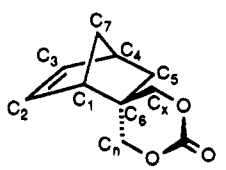


Figure 3. (A) ^{13}C NMR spectra of (A) 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (1), (B) poly[5,5-(bicyclo-[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one] [poly(1)], and (C) the cyclic oligmers of 5,5-bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one.



while after dilution and equilibration, oligomers are the main product (Figure 1b). The oligomers represent a homologous series as indicated by the straight line (Figure 4) obtained when the logarithm of the degree of polymerization of the individual oligomers is plotted against their elution volume as taken from Figure 1b. ^{13}C NMR analysis of the oligomeric mixture (Figure 3C) reveals for each kind of carbon atom several signals, with one

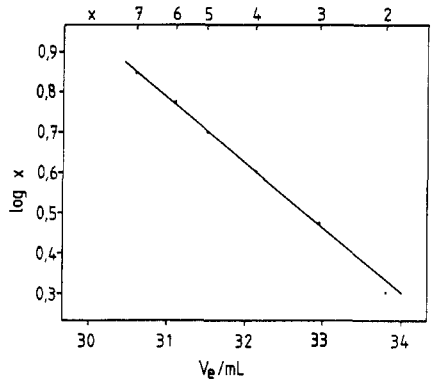


Figure 4. GPC calibration curve. Plot of $\log_{10} x$ vs elution volume (V_e) of the homologous series of cyclic oligomers of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (x, degree of oligomerization).

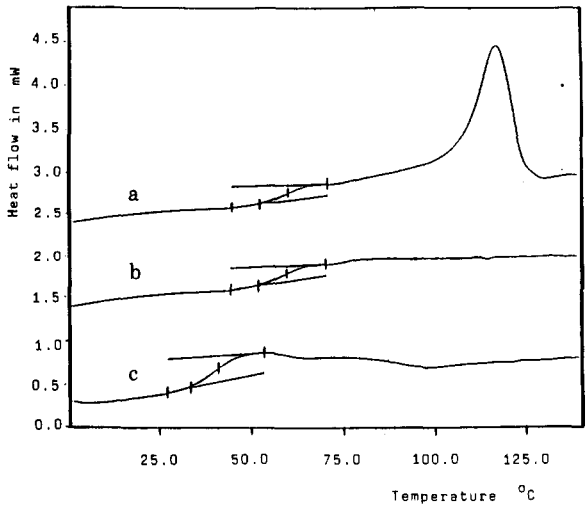
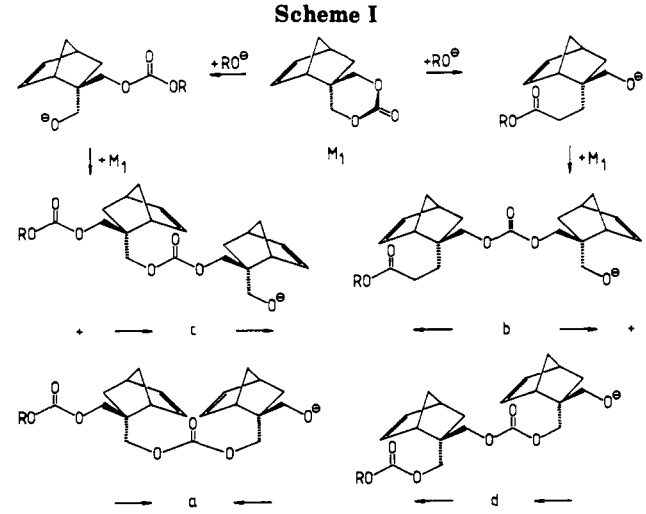


Figure 5. DSC curves of poly[5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one]. (a) First heating of a sample precipitated in methanol; (b) second heating of the aforementioned sample; (c) first heating of a polymer film sample as cast from a methylene chloride solution.

exception—the carbonyl carbon atom—shows only one signal at δ = 154.9 ppm. This finding is in accord only with a uniform exo–endo structure of the carbonate moieties within the cyclic oligomers. The formation of these cyclics during equilibration/depolymerization must be a complicated process including transesterification with selective formation of only exo–endo-linked monomer units at the chain end, which then can given backbiting reactions with formation of cyclic oligomers. With a statistical sequence of exo–exo-, exo–endo-, endo–endo-linked monomer units the backbiting probability is extremely low, since cyclic oligomers with high ring strain would arise.

The thermal behavior of the poly[5,5-(bicyclo[2.2.1]-hept-2-en-5,5-ylidene)-1,3-dioxan-2-one] is determined by the prehistory of the sample. A sample precipitated in methanol shows upon the first heating (heating rate 20 °C/min) a T_g at 60 °C and a T_m at 117 °C (Figure 5a), on cooling at 20 °C/min no crystallization is observed. Upon the second heating only a T_g at 60 °C (Figure 5b) is found. Even upon annealing for ca. 1 h at 70 °C no crystallization occurred. On the other hand, a polymer film casted from methylene chloride shows a T_g at 35 °C (Figure 5c). This depression of the T_g value is explained by the presence of residual methylene chloride, which even after prolonged drying at high vacuum and a temperature of 50 °C could not be removed. An elemental analysis of the polymer showed a chlorine content of 2.1%, indicating the presence

Scheme I



of 1 methylene chloride molecule per 18 repeating units. The relatively high T_g of the polymer compared, for example, with poly[(5-(allyloxy)methyl-5-ethyl)-1,3-dioxan-2-one] (T_g = −29 °C) or poly(5,5-dimethyl-1,3-dioxan-2-one) (T_g = +27 °C) is easy explained by the relative high stiffness introduced by the norbornene system linked to the polymer backbone via a spiro bond.

The atactic arrangement of the norbornene moiety, however, prevents crystallization of the polymer. This phenomenon was also observed with polymethacrylates; atactic poly(methyl methacrylate) exhibits a T_g at 100 °C, while the T_g of poly(adamantyl methacrylate) is 141 °C.

Copolymerization of 5,5-(Bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one and 5,5-Dimethyl-1,3-dioxan-2-one. In previous papers on the copolymerization of 5,5-dimethyl-1,3-dioxan-2-one (**2**) with 5-[(allyloxy)-methyl]-5-ethyl-1,3-dioxan-2-one (**3**),[2] ϵ-caprolactone,[3] and pivalolactone,[4] we have shown that statistical, tapered, or block copolymers may be obtained because of the different reactivities of the monomers when a mixture of two monomers is treated with the initiator. In the present case we were interested in seeing whether large differences in the bulkiness of the substituent induce different polymerization rates of the 1,3-dioxan-2-one system.

Two procedures were used for the copolymerization of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (**1**) with 5,5-dimethyl-1,3-dioxan-2-one (**2**). In procedure A, a solution of both monomers was treated with the initiator. From this procedure the formation of a random copolymer is expected. In procedure B, first a solution of monomer **1** was treated with the initiator and after consumption of the monomer a solution of monomer **2** was added. Under these reaction conditions the formation of a block copolymer is expected. A prerequisite is that the reaction conditions are unfavorable for transesterification reactions as compared with the propagation (chain growth) reaction. In both procedures the ratio of the monomers employed is identical with the ratio of repeating units in the polymers. The time–conversion diagram (Figure 6) shows that in the beginning of the reaction the conversion of 5,5-dimethyl-1,3-dioxan-2-one is slightly favored over that of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one. This difference in reactivity is to be attributed to the steric influence of the bulky norbornene substituent, which shields the carbonyl group at least partially against a nucleophilic attack of the active species. A decisive proof for the polymer structure came from ^{13}C NMR analysis. Figure 7 shows the carbonyl region of both poly(**1**) and poly(**1**-*stat*-**2**). As

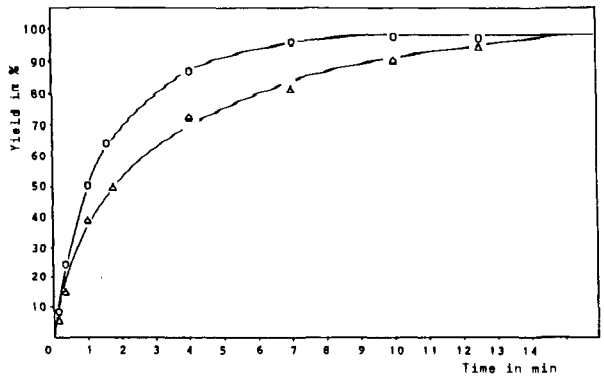


Figure 6. Polymerization of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one and 5,5-dimethyl-1,3-dioxan-2-one in toluene with *sec*-BuLi as initiator: dependence of monomer consumption on time. $[1]_0 = 0.63$ mol/L; $[2]_0 = 0.63$ mol/L; $[I]_0 = 0.35$ mmol/L; $T = 0$ °C. A preparation technique: the initiator is added to a mixture of the monomers, 1 (△), 2 (○).

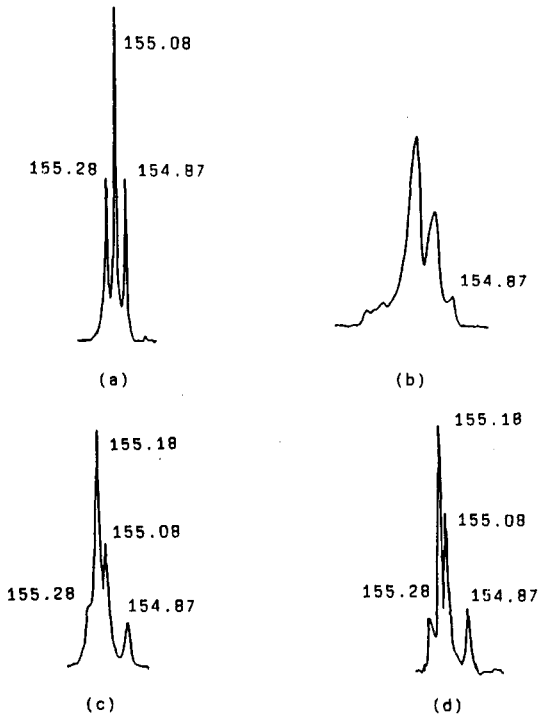


Figure 7. ^{13}C NMR spectrum of the the carbonyl region of (a) poly(1), (b) poly(1-*stat*-2), (c) poly[1-*block*-2], and (d) a blend of poly(1) and poly(2).

mentioned before, the signals in (a) represent the three possible types of carbonyl carbon atoms in the homopolymer 1, viz., the exo–exo- and endo–endo-linked carbonate groups, assigned to the minor signals and the exo–endo- respective endo–exo-linked carbonate groups, which are magnetically equal and are assigned to the resonance at $\delta = 155.08$ ppm. The ratio of the three signals is 1:2:1. The signals in Figure 7b are broad and unresolved beside the signal at $\delta = 154.87$ ppm which was assigned to the exo–exo- (or endo–endo-) linked carbonate groups. Assuming a statistical copolymer of equimolar amounts of 1 and 2 and Bernoullian statistics, the probabilities of possible diads are shown in Table I. From these probabilities the ratio of the diad XX to the other diads is 1:15. The area of the signal at δ 154.87 ppm (Figure 7b) was assigned to the diad XX and hence was related to the area of the resonance integrals of the other carbonyl carbon atoms which represent the sum of the unresolved diads of the system. The ratio of these areas was determined to be 1:13.1. This result shows that homodiads occur more

Table I
Probabilities of the Diads in a Statistical and a Block Copolymer of 1 and 2[a]

	diad[c]								
copolymer	NN	XN	NX	XX	CN	NC	CX	XC	CC
statistic[b]	1	1	1	1	2	2	2	2	4
block	1	1	1	1					4

[a] Molar ratio of [1]:[2] = 1. [b] Bernoullian statistics assumed. [c] N represents the endo side of monomer 1; X represents the exo side of the monomer 1; C represents monomer 2.

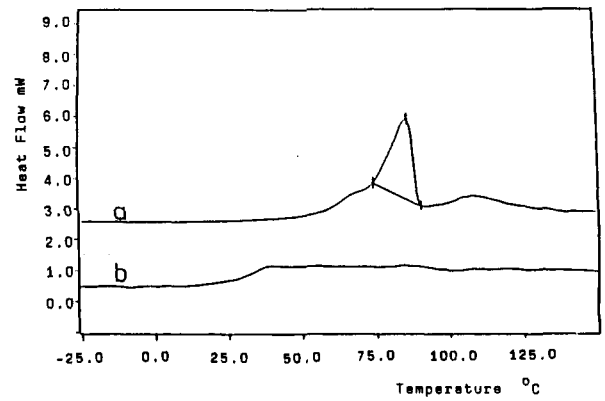


Figure 8. DSC curve of poly[5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one-*block*-5,5-dimethyl-1,3-dioxan-2-one]. (a) First heating; (b) second heating.

frequently, as expected according to Bernoullian statistics. This is in agreement with the time conversion curve, which shows that 2 in the beginning of the reaction is incorporated with a higher rate than 1 thus favoring homodiads over heterodiads.

The copolymer obtained via procedure B has a blocky structure. Figure 7c shows four resolved signals in the carbonyl region; the signals at $\delta = 154.87$, 155.08, and 155.28 ppm are assigned to the diads XX, XN, or NX and NN for monomer 1, respectively, and the signal at $\delta = 155.18$ ppm is assigned to a homodiad of monomer 2. A blend of poly(1) and poly(2) with an equimolar ratio of repeating units results in virtually the same spectrum (Figure 7d), although the resolution of the signals of the blend is better than that of the block copolymer. The ratio of a diad XX to the other possible diads for a block copolymer is 1:7 (Table I). The ratio of the area of the signal at $\delta = 154.87$ ppm to the sum of the areas of the other signals yields a value of 1:6.9, in good agreement with the theoretical value. The statistical copolymer with a molar ratio of the monomer units equal to 1 exhibits a T_g of 13 °C. This value is lower by 34 °C than expected from the Fox equation (eq 1), where w_2 represents the weight fractions

$$\frac{1}{T_g} = w_2\left(\frac{1}{T_{g_1}} - \frac{1}{T_{g_2}}\right) + \frac{1}{T_{g_1}} \qquad (1)$$

of the monomer and T_{g_1} and T_{g_2} the glass transition temperatures of the respective homopolymers. The reason for the low experimental value of T_g is attributed to the large difference in steric requirements of the two monomers.

A block copolymer with the same composition upon first heating shows a T_g of 60 °C and two melting transitions at 85 and 110 °C (Figure 8a). While the melting transitions cannot be assigned, the T_g has to be assigned to the poly(1) block. Upon second heating only one T_g value at 30 °C is observed, indicating a mixed phase. The thermal behavior of a blend of poly(1) and poly(2) with the same composition as the block copolymer exhibits a completely

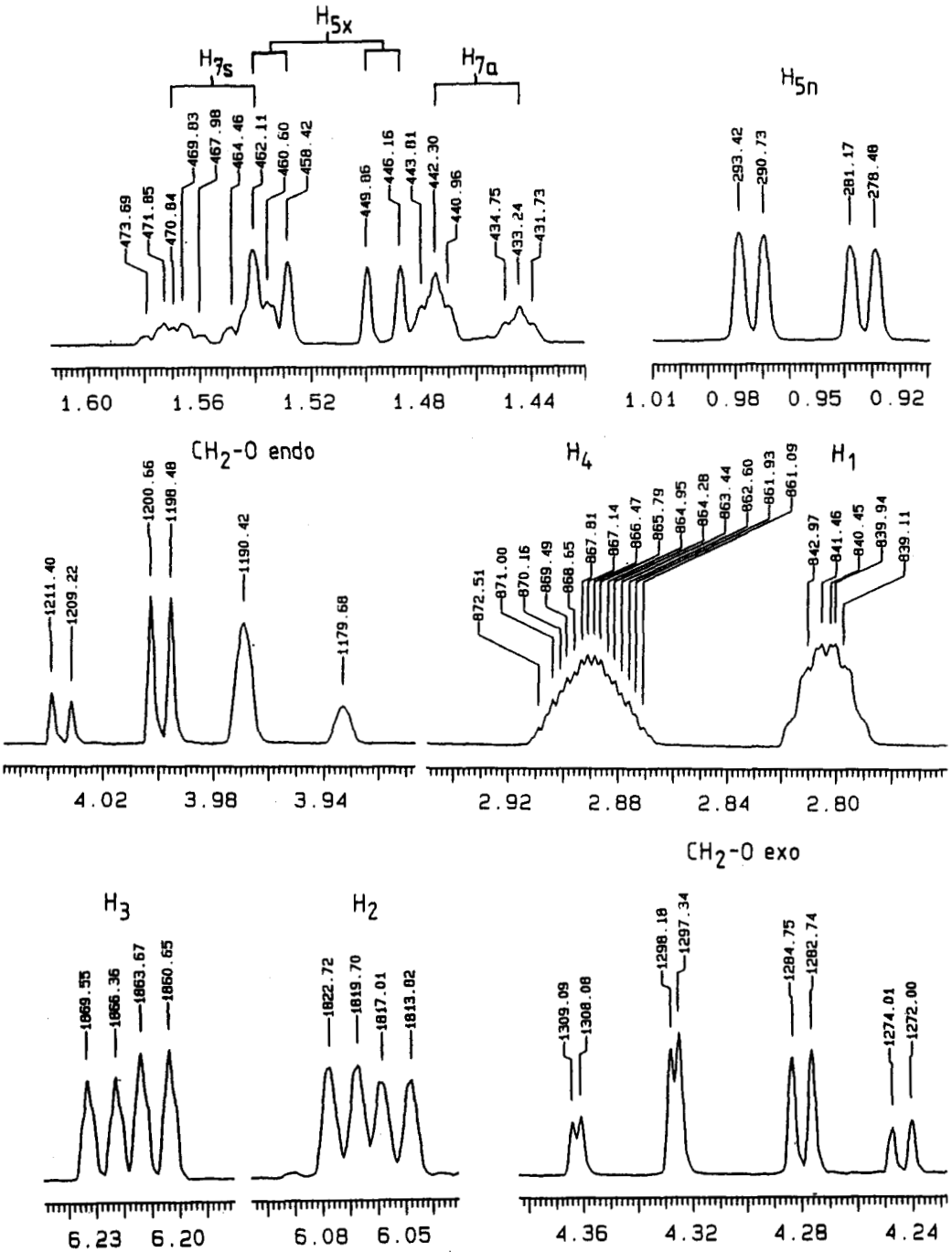


Figure 9. ^{1}H NMR spectrum of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one.

different thermal behavior. Upon first heating three melting transitions are observed, two for poly(2) at 79 and 120 °C and one at 102 °C assigned to poly(1).

Experimental Section

Reagents. 5,5-(Bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (1) and 5,5-dimethyl-1,3-dioxan-2-one (2) (both from Bayer AG) were purified before use by sublimation. Toluene was freshly distilled from a solution of *sec*-butyllithium. *sec*-Butyllithium (1.4 M solution in cyclohexane/isopentane from Aldrich Chemical Co.) was used as initiator without further purification. Nitrogen and argon (both from Linde) were passed over molecular sieves (4 Å), finely distributed potassium on aluminum oxide, and reduced Phillips catalyst 800/350 (Cr(II) on silica gel) for purification.

^{1}H NMR Spectrum of 5,5-(Bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one. Figure 9 shows the expanded ^{1}H NMR spectrum of 1. The assignments were made on the basis of double-resonance experiments, 2D spectra, and coupling constants. These assignments were also adopted for the polymer.

General Polymerization Procedure. All glass vessels were heated in vacuo before use, filled with inert gas, and handled in a stream of dry inert gas.

(a) Poly[5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one] [Poly(1)]. To 10 g (0.056 mol) of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one in 100 mL of toluene at room temperature was added 0.15 mL of a 1.4 M solution of *sec*-butyllithium; then the solution was cooled to 0 °C. After 3 h, the polymer solution was poured into 200 mL of methanol—containing phosphoric acid for neutralization—and kept at −30 °C for complete separation of the polymer. After filtration and drying, 9.81 g (0.054 mol) of polymer was obtained. ^{1}H NMR ($CDCl_3$): δ 6.18 (m, H_3), 6.06 (m, H_2), 4.22 (m, CH_2O_{exo}), 4.04 (m, CH_2O_{endo}), 2.86 (s, H_4), 2.73 (s, H_1), 1.51 (m, H_{7s}, H_{5x}, H_{7a}), 0.89 (m, H_{5n}) ppm. ^{13}C NMR ($CDCl_3$): δ 155.284 (endo, endo OC(O)O), 155.08 (endo, exo OC(O)O), 154.87 (exo, exo OC(O)O), 137.84 (C_3), 134.06 (C_2), 70.9 (C_X), 70.1 (C_N), 47.11 (C_7), 46.30 (C_6), 45.84 (C_1), 42.36 (C_4), 32.59 (C_5) ppm.

(b) Poly[5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one-*stat*-5,5-dimethyl-1,3-dioxan-2-one]. To 3.6 g (0.02

mol) of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one and 2.6 g (0.02 mol) of 5,5-dimethyl-1,3-dioxan-2-one in 50 mL of toluene at −5 °C was added 0.06 mL of a 1.4 M solution of *sec*-butyllithium. After 3 h, the polymer was obtained in 80% yield. ^{1}H NMR ($CDCl_3$): δ (the resonances for 2,2-dimethyltrimethylene–carbonate repeating units are marked as M_2) 6.18 (m, H_3), 6.06 (m, H_2), 4.24 (m, CH_2O_{exo}), 3.93 (m, CH_2O_{endo} and for (M_2) CH_2O, 4 H), 2.86 (s, H_4), 2.73 (s, H_1), 1.54 (m, H_7, H_{5x}, H_{7a}), 0.98 (s, (M_2) CH_3, 6 H), 0.88 (m, H_{5n}) ppm. ^{13}C NMR ($CDCl_3$): δ 155.3–154.9 (OC(O)O several signals; see Results and Discussion), 137.9 (C_3), 134.1 (C_2), 72.5 (CH_2O (M_2), 2 C), 70.9 (C_X), 70.2 (C_N), 47.2 (C_7), 46.4 (C_6), 45.9 (C_1), 42.4 (C_4), 32.7 (C_5), 35.2 ($C_{quatern}$, (M_2) 1 C), 21.4 (CH_3, (M_2) 2 C) ppm.

(c) Poly[5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one-*block*-5,5-dimethyl-1,3-dioxan-2-one]. To 7.2 g (0.04 mol) of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one in 70 mL of toluene at 0 °C was added 0.25 mL of a 1.4 M solution of *sec*-butyllithium. After 3 h, a solution of 5.2 g (0.04 mol) of 5,5-dimethyl-1,3-dioxan-2-one in 50 mL of toluene was added and the resultant mixture was subjected to polymerization for another 3 h. The block copolymer was obtained in 92% yield.

The ^{1}H and ^{13}C NMR show all signals of the homopolymers and no additional resonances.

Determination of the Time–Conversion Plot (Figure 4). Samples from the polymerization mixture were quenched with methanolic phosphoric acid at different times, followed by evaporation of the solvent, and analysis of the residue by ^{1}H NMR spectroscopy.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker CXP-220 FT-NMR spectrometer at 220 and 50 MHz, respectively. Deuteriochloroform was used as solvent and TMS as internal standard.

Thermoanalytical measurements were recorded on the differential scanning calorimeter DSC-7 (Perkin-Elmer). Each sample was heated from −100 to +150 °C (first heating cycle), cooled immediately to −100 °C, and heated again to +150 °C (second heating cycle). The heating and cooling rates were 20 K/min.

GPC analyses were carried out using a Waters apparatus with a combined UV and RI detector. For the separation, a combination of four columns was applied with PL-gel (from Polymer Laboratories): length 300 mm, diameter 7.0 mm, diameter of the gel particles 5 μm, pore width 100, 500, 10^3, and 10^4 Å. In all cases, THF was the eluting solvent with a flow rate of 0.5 mL/min. For calibration polystyrene standards were used.

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References and Notes

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