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Synthesis of polymers having 1,3-cyclobutanedione unit in the main chain by cycloaddition polymerization of bisketene

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Summary

A novel polymer having 1,3-cyclobutanedione unit in the main chain was prepared by cycloaddition polymerization of the bisketene derived from 1,4-cyclohexanedicarbonyl chloride. The polymer was soluble in MeOH, acetone, and $CHCl_3$. The structure of the polymer was confirmed by IR, ^1H-, and ^{13}C-NMR spectroscopies compared with those of the model compounds. The polymer was found to contain anhydride bond as well as 1,3-cyclobutanedione unit in the main chain. The anhydride bond in the polymer was cleaved by MeOH under reflux condition in benzene.

Introduction

Ketenes and bisketenes can be used as monomers in several different types of polymerizations [1]. Polyesters and polyamides have been prepared by polyaddition of bisketenes with diamines and diols, respectively [2]. Recently, novel polymers having 2-azetidinone structure prepared by [2 + 2] cycloaddition of bisketene with bisimine were reported [3].

The most important ketene reaction might be its dimerization. With few exceptions, all ketenes dimerize upon standing at room temperature or on heating for short time. The dimerization of ketene is regarded as a ($_{\pi}2_s+_{\pi}2_a$) concerted process with a high negative entropy of activation and little solvent polarity dependance [4]. Despite popularity of the reaction, polymer syntheses by using dimerization of bisketenes have been limited so far [5]. To our knowledge, dimer to pentamer isolated by the reaction of bisketene was the only reported example [5b]. However, the characterization of the polymer product was not sufficient. Thus, we focused here our attention on polymerization via dimerization of bisketenes to afford polymers having 1,3-cyclobutanedione unit.

Spiropolymers are interesting materials for their peculiar polymer backbones. Their thermal and chemical stabilities are enhanced compared to the corresponding linear polymers. If a cyclic bisketene was employed as a monomer, a new spiropolymer having 1,3-cyclobutanedione unit would be obtained. Here, we wish to report the synthesis of new spiropolymers having 1,3-cyclobutanedione unit in the main chain via dimerization of the bisketene derived from 1,4-cyclohexanedicarbonyl chloride.

Results and Discussion

The polymerization of the bisketene was carried out as follows in various organic solvents. In this system, the bisketene which could not be isolable was directly generated from 1,4-cyclohexanedicarbonyl chloride **1** *in situ*. To a solution of **1** was added 3 equivalent of dry triethylamine at 0 °C. After stirring at 0 °C for 3 h, the reaction mixture was heated at appropriate temperature to effect the polymerization. Finally, MeOH was added for end-capping of the polymer and the mixture was stirred for 30 min at room temperature. The precipitated triethylamine hydrochloride was filtrated, and the filtrate was poured into *n*-hexane. After the obtained precipitate was dried under reduced pressure, a brown polymer was obtained. The polymer was soluble in MeOH, acetone and $CHCl_3$, insoluble in THF and Et_2O. Table 1 shows the results of polymerization in various solvents. The highest molecular weight of the polymer was obtained when benzene was used as a solvent. Although yields of the polymer were high in CH_2Cl_2 and CH_2ClCH_2Cl,

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the molecular weights of the polymers were decreased.

Scheme 1

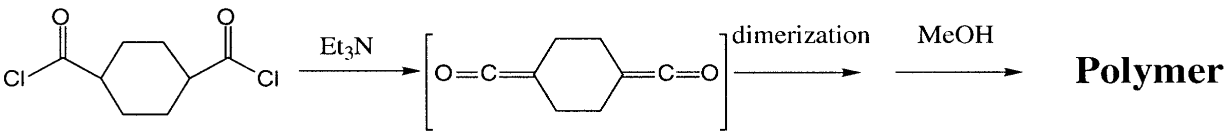

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Table 1. Polymerization of 1,4-Cyclohexanedicarbonyl Chloride in Various Solvents [a)]

run	solvent	reaction temp.(°C)	yield(%)	M_w [b)]	M_n [b)]	M_w/M_n [b)]
1	Et_2O	reflux	18	3,700	800	4.6
2	C_6H_6	reflux	29	10,300	2,300	4.5
3	toluene	90	34	4,800	1,300	3.8
4	CH_2Cl_2	reflux	43	3,300	1,300	2.5
5	CH_2ClCH_2Cl	reflux	57	2,100	1,000	2.1
6	CH_3CN	reflux	6	7,000	3,300	2.1

a) Et_3N was 3eq, reaction time was 48h b) Determined by GPC ($CHCl_3$, PSt standard)

Table 2. Polymerization of 1,4-Cyclohexanedicarbonyl Chloride in Benzene

run	Et_3N	reaction temp.(°C)	reaction time (h)	yield(%) [a)]	M_w [b)]	M_n [b)]	M_w/M_n [b)]
1	3eq	r.t.	48	21	1,000	500	2.0
2	3eq	50	48	31	2,500	1,000	2.5
3	3eq	reflux	48	29	10,300	2,300	4.5
4	3eq	reflux	120	40	34,500	6,400	5.4
5	10eq	reflux	120	20	8,400	4,100	2.1

a) Isolated yields b) Determined by GPC ($CHCl_3$ PSt standard)

Table 2 summarizes the results of polymerization under various conditions using benzene as a solvent. When the polymerization was carried out at higher temperature and for the longer time, the molecular weight of the resulting polymer in GPC was shifted to a higher molecular weight region (Figure 1). Adding 10 equivalent of triethylamine decreased both the molecular weight and the yield of the polymer (run 5).

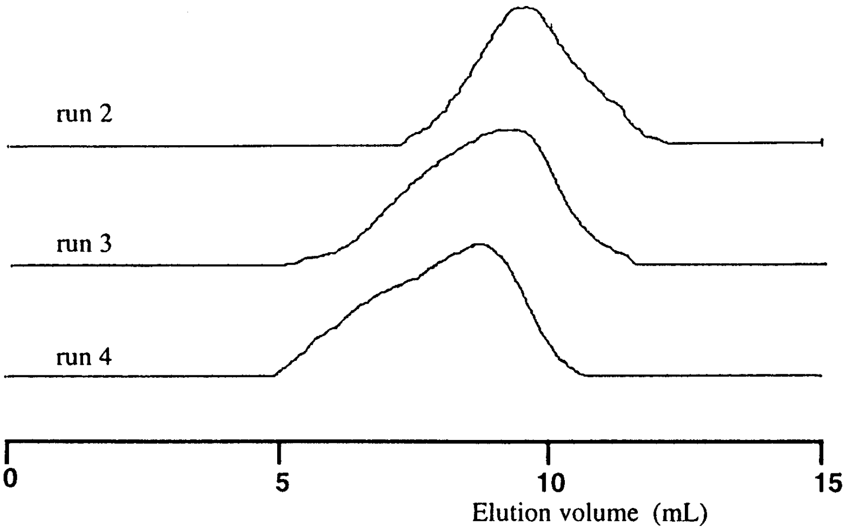
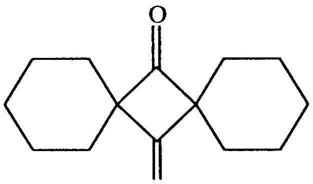


Figure 1. GPC charts of polymers obtained from run 2, 3, and 4 in Table 2.

The structure of the obtained polymer was confirmed by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopies compared with dispiro[5,1,5,1]tetradecane-7,14-dione **2** as a model compound [7], which was obtained by treatment of cyclohexanecarbonyl chloride with an excess amount of triethylamine. A model compound for the terminal methyl ester (**3**) was also prepared. The IR spectrum of the polymer exhibited a strong peak at 1732 cm^{-1}, which was assignable C=O vibration of the 1,3-cyclobutanedione unit. In the ^{13}C-NMR spectrum of the polymer, the peak for the keto carbon appeared at 213 ppm, along with the peak for the spiro carbon at 74 ppm. The same peaks originated from dispiro substituted 1,3-cyclobutanedione structure were confirmed in the ^{13}C-NMR spectrum of **2** at 215 and 75 ppm, respectively. Shoulder peaks at 1772 and 1808 cm-1 were observed in the IR spectrum of the polymer. These two peaks would be attributed to an anhydride linkage which was supposed to be derived from carboxlic acid resulted from hydrolysis of **1**. The peaks at 175 and 173 ppm were also observed in the ^{13}C-NMR spectrum of the polymer. The former was assigned to the keto carbon of the terminal methyl ester, which was based on the fact that the peak for the carbonyl carbon of **3** appeared at 176 ppm. The latter corresponded to the anhydride linkage. These results indicate that the obtained polymer contained two components, i.e., 1,3-cyclobutanedione and anhydride structures **4**.



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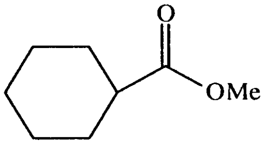

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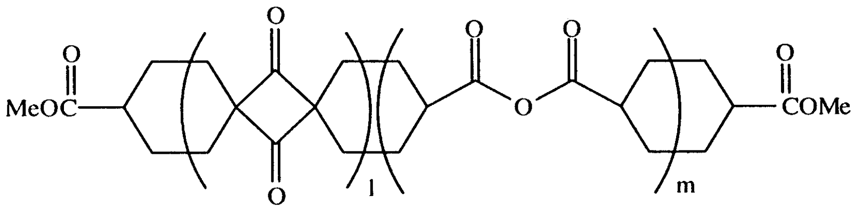

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The ^{1}H-NMR spectrum of the polymer 4 showed a broad peak from 1.4 to 2.6 ppm attributed to the cyclohexyl protons and a sharp peak for the terminal methyl protons at 3.6 ppm. The methine resonance at 2.0—2.6 ppm due to the terminal methyl ester and the anhydride moiety was observed in a shoulder of the broad resonance at 1.4—2.0 ppm assigned to the methylene protons of the cyclohexyl unit. The comparison of the peak areas of the methylene protons with those of the methine protons results in the estimation of the unit ratios 1 : 1.

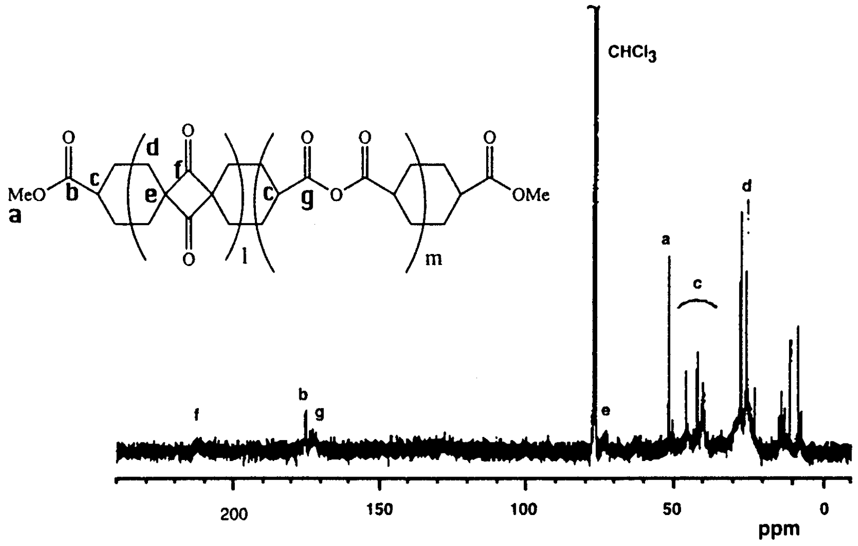

Figure 2. ^{13}C-NMR spectrum of 4.

The anhydride bond in the polymer might be labile against nucleophilic reagents. We tried to cleave the anhydride moiety in 4 by MeOH as follows. After adding an excess amount of MeOH for end-capping of the polymer, a half portion of the reaction mixture was filtrated to remove amine hydrochloride. The filtrate was poured into water, and extracted with CH_2Cl_2. The combined organic fractions were evaporated to obtain the polymer 4a. The remained reaction mixture was heated under reflux for 3.5 h to effect cleavage reaction. The reaction mixture was worked up in a similar manner as described above to give the polymer 4b.

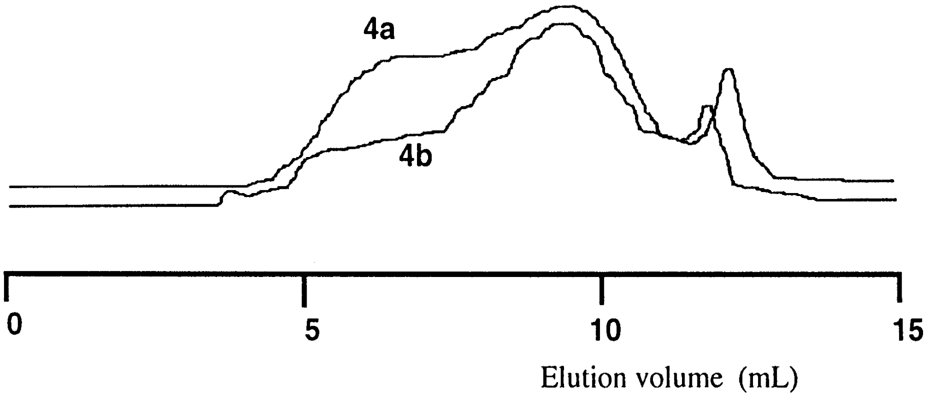

Figure 3. GPC charts of polymers before (**4a**) and after (**4b**) reaction with MeOH.

The GPC measurements for 4a and 4b are shown in Fig.3. The number-average molecular weight of 4b(M_n = 3,000) was lower than that of 4a(M_n = 2,500). This indicates a degradation of the polymer backebone occurred during reaction with MeOH. The IR spectrum of **4b** showed relatively weak peaks at 1772 and 1808 cm^{-1} compared with those of **4a**. The weak peaks indicated the cleavage of the anhydride moiety. Although a part of the anhydride linkage disappeared, the peak at 173 ppm assignable to the anhydride carbonyl carbon was still observed in the ^{13}C NMR spectrum even if refluxing time was extended up to 8h.

Thermogravimetric analysis (TGA) was recorded for 4 under nitrogen. The small weight loss of the polymer started at 130 °C. Subsequently, a rapid weight loss began at about 210°C and was completed at 510 °C.

In conclusion, we synthesized the polymer 4 having 1,3-cyclobutanedione unit by dimerization of the bisketene derived from 1,4-cyclohexanedicarbonyl chloride 1. Although the polymer 4 contained the anhydride unit in the main chain, the resulting polymer can be regarded as a novel type of reactive polymers owing to lability of the anhydride bond as well as the 1,3-cyclobutanedione unit.

Experimental Section

General. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. 1,4-Cyclohexanedicarbonyl chloride was prepared from 1,4-cyclohexanedicarboxylic acid by the reported method [8].

^{1}H-and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a JEOL EX-270 instrument. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Gel permeation chromatography was carried out on a Shodex K-803 by using chloroform as an eluent after calibration with standard polystyrene samples. Thermogravimetric analysis was made on a Shimadzu DT-30 instrument (10 °C/min).

Dispiro[5.1.5.1]tetradecane-7,14-dione 2. 2 was prepared by the reported method [7]. IR (NaCl) 2937, 2852, 1734 (C=O), 1447, 1299, 1183 cm^{-1}; ^{1}H-NMR ($CDCl_3$) (δ, ppm) 1.40-1.55 (m, 4H), 1.57-1.81 (m, 16H); ^{13}C-NMR ($CDCl_3$) (δ, ppm) 22.5, 25.6, 29.3, 74.7, 215.4.

Methyl cyclohexanoate 3. To a benzene solution (15 ml) of cyclohexanecarbonyl chloride (1.47 g, 10 mmol) was added an excess amount of dry triethylamine (3 equivalent, 3.04 g, 30 mmol). After stirring at room temperature for 30 min, MeOH (0.48 g, 15 mmol) was added and the mixture was stirred for 1.5 h. After the precipitated amine hydrochloride was filtrated, water was added and the residue was extracted with Et_2O. The organic layer was dried ($MgSO_4$) and evaporated to give the product (108 mg, 76 %). ^{1}H-NMR ($CDCl_3$) (δ, ppm) 1.05-1.81 (m, cyclohexyl, 10H), 2.18 (m, cyclohexyl, 1H), 3.55 (s, $-COCH_3$, 3H); ^{13}C-NMR ($CDCl_3$) (δ, ppm) 24.9, 25.4, 28.7, 42.7, 50.9, 176.0.

Polymerization. A typical procedure is as follows. To a benzene solution (1.0 ml) of 1,4-cyclohexanedicarbonyl chloride (157 mg, 0.75 mmol) was added an excess amount of dry triethylamine (3 equivalent, 0.32 ml, 2.25 mmol) at 0 °C. After stirring at 0°C for 3 h, the reaction mixture was heated at reflux condition to effect the polymerization. Finally, MeOH (0.1 ml) was added for end-capping and the mixture was stirred for 30 min. The precipitated amine hydrochloride was filtrated, and the filtrate was poured into *n*-hexane (50 ml). The precipitate was dissolved in CH_2Cl_2 (1 ml) and the solution was washed with 0.1N HCl (2 ml). The organic layer was poured into *n*-hexane (50 ml). After the obtained product was dried under reduced pressure, a brown polymer was obtained (41 mg, 40 % yield). IR (NaCl) 2932, 2855, 1808 (sh), 1772 (sh), 1732, 1453 cm^{-1}; ^{1}H-NMR ($CDCl_3$) (δ, ppm) 1.4-2.6 (m, cyclohexyl), 3.61 (s, $-COCH_3$); ^{13}C-NMR ($CDCl_3$) (δ, ppm) 23.0, 24.4, 25.8, 27.8, 40.1, 42.3, 51.5, 73.7, 173.0, 175.2, 213.4.

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