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S. Kobayashi[a]; J. Kadokawa[a]; Y. Matsumura[a]; I. F. Yen[a]; H. Uyama[a]
[a] Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba, Sendai, Japan

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RADICAL COPOLYMERIZATION OF 2-METHYLENE-1,3-DITHIANE WITH STYRENE AND METHYL METHACRYLATE

S. Kobayashi,* J. Kadokawa, Y. Matsumura, I. F. Yen, & H. Uyama

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba, Sendai 980, Japan

ABSTRACT

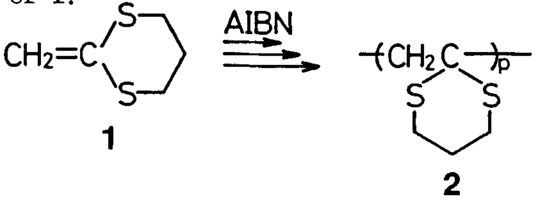
This paper describes radical copolymerization of 2-methylene-1,3-dithiane (a six-membered cyclic ketene dithioacetal, **1**) with styrene and methyl methacrylate (MMA). The copolymerization proceeded without ring-opening of **1** to produce copolymer having dithioacetal group. The structure of the copolymer was determined by ^1H, ^{13}C NMR, IR, and UV spectroscopies. Polymerizability of **1** was higher than that of styrene and MMA. Monomer reactivity ratios determined are r_1 = 3.35 and r_2 = 0.03 (M_2 = styrene) or r_1 = 4.12 and r_2 = 0.08 (M_2 = MMA). The refractive index values of the resulting copolymers were also measured.

INTRODUCTION

Organic synthesis using organosulfur compounds has been developed as quite interesting synthetic methods.[1] However, there have not been so many examples which apply this organosulfur chemistry to the polymer synthesis field. Especially, polymerization of vinyl compounds containing sulfur atom has not been studied well.

Polymerization of cyclic ketene acetals has been extensively studied by Bailey et al.[2] The polymerization , however, proceeded involving partly ring-opening of the monomer to give a polymer having a ketene acetal unit and an ester unit. Therefore, polymers exclusively with a cyclic acetal unit have not synthesized. In order to introduce a dithioacetal group in the polymer chain, we have already examined radical polymerization of

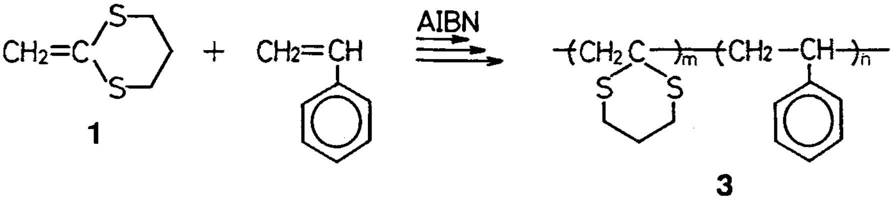
2-methylene-1,3-dithiane (a six-membered cyclic ketene dithioacetal, **1**).[3] The polymerization proceeded to give polymer **2** possessing dithioacetal unit by vinylidene polymerization without ring-opening of **1**.



The molecular weight of **2** obtained by solution polymerization, however, was relatively low. On the other hand, bulk polymerization of **1** gave a polymer insoluble in all organic solvents examined. This may be because the insoluble polymer has higher molecular weight. In order to obtain a soluble polymer having a dithioacetal group of high molecular weight, radical copolymerization of **1** with styrene and with methyl methacrylate (MMA) was carried out.

RESULTS AND DISCUSSION

Copolymerization of **1** with styrene. Copolymerization was carried out with AIBN as a radical initiator in bulk at 80 °C under argon. A usual work-up gave a white powderly material. It is soluble in $CHCl_3$, benzene, and toluene, but insoluble in n-hexane, methanol, and water. The gel permeation chromatographic (GPC) analysis of the product showed only one peak, indicating that **1** was copolymerized with styrene to form a copolymer.



The structure of copolymer (**3**) was determined by ^1H, ^{13}C NMR, IR, and UV spectroscopies. The ^1H NMR spectrum of the copolymer (entry 1 in Table I) in $CDCl_3$ showed three peaks at δ 1.0-2.2 (broad, C-CH_2-C and -CH-), 2.2-3.9 (broad, S-CH_2), and 7.28 (broad s, -C_6H_5). The data supports the structure of the copolymer was **3**. The copolymer composition of **1** and styrene in **3** was calculated to be 47:53 by the integrated ratio of S-CH_2 signal and phenyl signal in the ^1H NMR spectrum. The copolymer

TABLE I
Copolymerization of **1** with Styrene[a]

entry	**1** (%)	styrene (%)	AIBN (mol%)	time (h)	yield[b] (%)	mol wt[c]	copolymer[d] composition **1** : styrene
1	50	50	3	24	67	3100	47 : 53 (48 : 52)[e]
2	50	50	5	2	43	2300	84 : 16
3	20	80	3	24	80	7000	19 : 81 (22 : 78)[e]
4	20	80	5	2	82	8500	18 : 82

[a] [1] + [styrene] = 2.5 mmol, at 80 °C. [b] n-Hexane insoluble part. [c] Determined by GPC with $CHCl_3$ at 40 °C. [d] Determined by ^1H NMR. [e] Determined by elemental analysis.

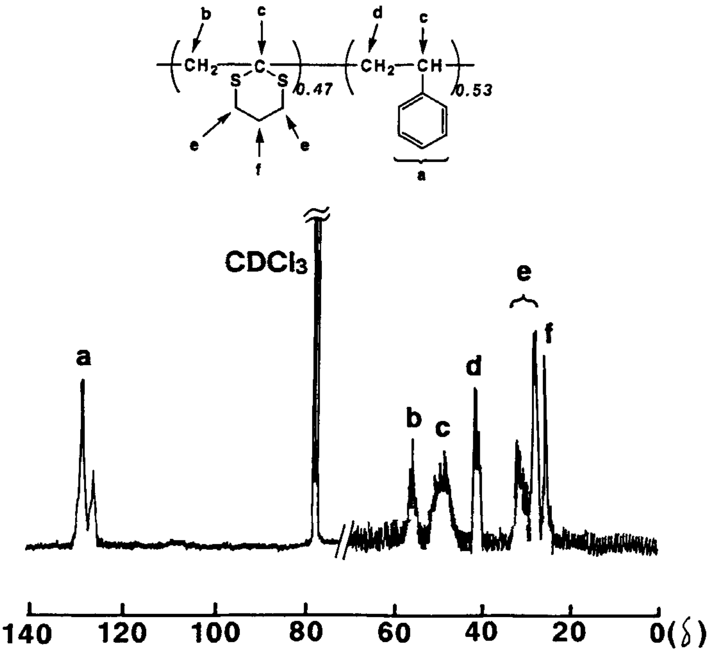


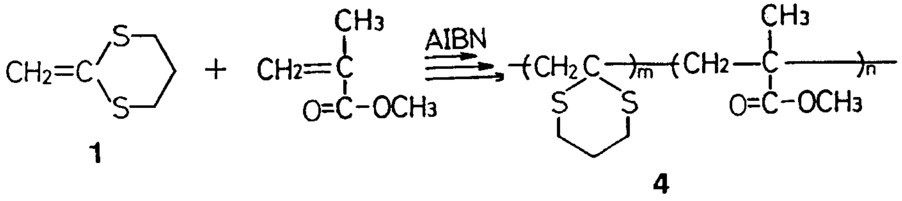
Figure 1. ^{13}C NMR Spectrum of Copolymer **3** (entry 1 in Table I) in $CDCl_3$.

composition was also calculated from the elemental analysis, which was very close to that obtained by the ^{1}H NMR analysis. Anal. Calcd for the 22:78 composition (1:styrene), $(C_{7.34}H_{8.00}S_{0.44})_n$ (entry 3 in Table I): C, 79.70; H, 7.24; S, 12.74. Found: C, 78.64; H, 7.13; S, 11.87.

Figure 1 shows the ^{13}C NMR spectrum of the copolymer (entry 1 in Table I) in $CDCl_3$. The assignment was as follows.[3,4] Peaks at δ 25.4 and 27.4 are due to methylene carbons in the ring from **1**. A peak at δ 41.4 is due to methylene carbon of the unit from styrene. A broad peak centered at δ 49.0 is due to quartarnary carbon and methyne carbon. A peak at δ 56.0 is due to methylene carbon in the main chain of the unit from **1**. Peaks at δ 126.4 and 128.7 are due to aromatic carbons. In addition, a peak due to thiocarbonyl carbon was not observed around δ 193. Furthermore, IR and UV spectra of the copolymer did not exhibit the absorption due to thiocarbonyl group at 1100 cm^{-1} and 470 nm, respectively. These spectroscopic data are also taken to support that the copolymerization proceeded without ring-opening of **1** to give the copolymer **3**.

Some copolymerization results are given in Table I. When the feed ratio of **1** and styrene was 50 : 50, the molecular weight of the copolymer was relatively low. On the other hand, when the feed ratio was 20 : 80, the molecular weight was much higher than that of homopolymer **2**.[3] The copolymer composition was in good agreement with the feed ratio except entry 2. In case of shorter polymerization time (entry 2), the yield was lower and the content from **1** in **3** was larger than the feed ratio, suggesting that the radical polymerizability of **1** is higher than that of styrene.

<u>Copolymerization of 1 with MMA.</u> Radical copolymerization of **1** with MMA was also carried out with AIBN as a initiator in bulk at 80 °C under argon. The product was a white powderly material, whose solubility was similar with that of the copolymer **3**. The GPC curve of the product showed one peak, suggesting the occurrence of copolymerization.



The structure of the copolymer **4** was confirmed by ^{1}H, ^{13}C NMR, IR, and UV spectroscopies. The ^{1}H NMR spectrum of the copolymer (entry 1 in Table II) in $CDCl_3$ showed a singlet peak at δ 1.60 due to C-CH_3, broad peaks at δ 1.0-2.5 due to C-CH_2-C,

TABLE II
Copolymerization of 1 with MMA[a]

entry	1 (%)	MMA (%)	AIBN (mol%)	time (h)	yield[b] (%)	mol wt[c]	copolymer[d] composition 1 : MMA
1	50	50	3	24	82	3300	52 : 48
							(51 : 49)[e]
2	40	60	5	2	41	2200	70 : 30
3	30	70	3	24	90	8600	26 : 74
							(30 : 70)[e]
4	20	80	5	2	46	2300	24 : 76
5	20	80	3	24	92	9700	19 : 81
							(22 : 78)[e]

[a] [1] + [MMA] = 2.5 mmol, at 80 °C. [b] n-Hexane insoluble part. [c] Determined by GPC with $CHCl_3$ at 40 °C. [d] Determined by ^1H NMR. [e] Determined by elemental analysis.

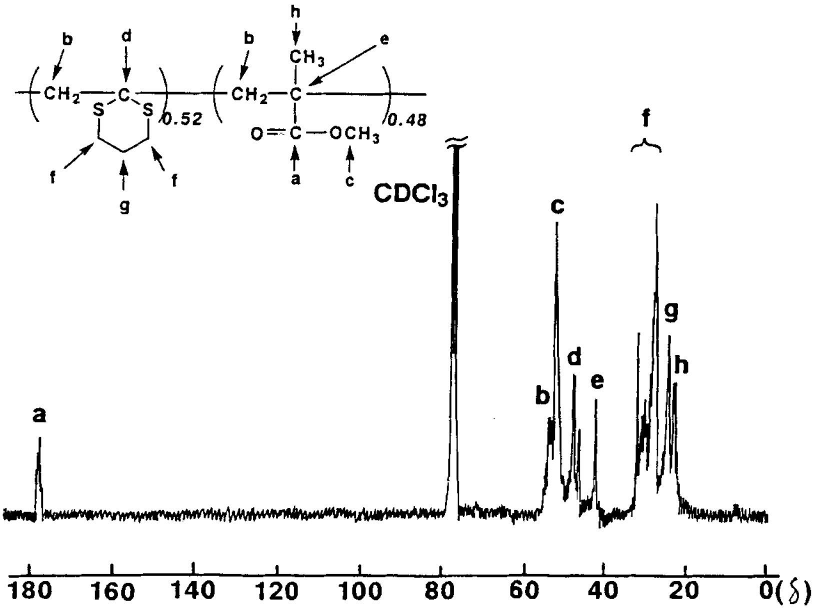


Figure 2. ^{13}C NMR Spectrum of Copolymer 4 (entry 1 in Table II) in $CDCl_3$.

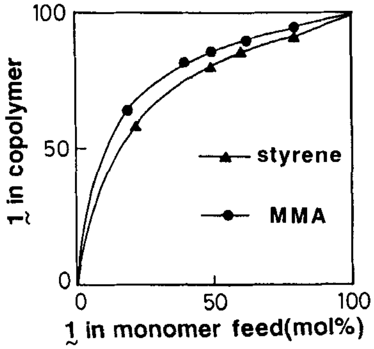


Figure 3. Copolymerization of **1** with styrene or MMA at 80 °C for 0.5 h. Polymer compositions at various comonomer feeds: [1] + [comonomer] = 2.5 mmol.

broad peaks at δ 2.5-3.9 due to S-CH_2, and a singlet peak at δ 3.63 due to O-CH_3. The copolymer composition was caclulated to be 52:48 by the integrated ratio of S-CH_2 signal and methoxy signal in the ^1H NMR spectrum, which was very close to that calculated from tne elemental analysis. Anal. Calcd for the 50:50 composition (1:MMA), $(C_5H_8SO)_n$ (entry 1 in Table II): C, 51.72; H, 6.90; S, 27.59. Found: C, 51.10; H, 6.81; S, 27.52.

The ^{13}C NMR spectrum of the copolymer (entry 1 in Table II) in $CDCl_3$ is shown in Figure 2. The assignment was as follows.[5] A peak at δ 22.9 is due to C-methyl carbon. Peaks at δ 24.2 and 27.6 are due to methylene carbons in the ring. Peaks at δ 42.1 and 45.8 are due to the quartarnary carbons of units from MMA and from **1**, respectively. Peak at δ 52.1 is due to methoxy carbon. A peak centered at δ 53.7 is due to methylene carbons in the main chain. A peak at δ 177.5 is due to carbonyl carbon. Furthermore, thiocarbonyl group was not observed in the ^{13}C NMR, IR, and UV spectra of the copolymer. All of these data support the copolymerization took place without ring-opening of **1** to yield the copolymer **4**.

Copolymerization results are shown in Table II. The molecular weight of the all copolymers was higher than that of homopolymer **2**.[3] The copolymer composition was in good agreement with the feed ratio except entry 2, which may be due to difference in polymerizability between **1** and MMA.

TABLE III
Refractive Indices of Copolymers

polymer structure	copolymer composition **1** : comonomer	mol wt	n_D[a]
2	100 : 0	1500	1.63
3	47 : 53	3100	1.62
3	19 : 81	7000	1.61
polystyrene	0 : 100		1.59-1.60[b]
4	52 : 48	3300	1.56
4	19 : 81	9700	1.52
polyMMA	0 : 100		1.492[b]

[a] Measured by an Abbe refractometer. [b] From ref 8.

Monomer Reactivity Ratio. Monomer reactivity ratios between **1** and styrene or MMA were determined. Copolymerization experiments were carried out with AIBN (5 mol% for monomer) in bulk at 80 °C for 0.5 h, which resulted in a low conversion. The copolymer was isolated and the copolymer composition was determined by ^1H NMR analysis. Figure 3 indicates that the polymerizability of **1** is higher than those of styrene or MMA. The monomer reactivity ratios are calculated by the integral method according to Mayo-Lewis[6] and obtained as $r_1 = 3.35$ and $r_2 = 0.03$ (M_2 = styrene) or $r_1 = 4.12$ and $r_2 = 0.08$ (M_2 = MMA). These results strongly indicate that copolymer **3** or **4** is rich in block segments; **1** was mainly consumed in the early stage of copolymerization and styrene or MMA was reacted mainly in the later stage. The ^{13}C NMR spectra (Figure 1 and 2) accord with this view.

Refractive Index of Copolymers 3 and 4. It has been well known that the refractive index of the compound containing sulfur atom is quite high according to Lorentz-Lorenz formula. The refractive index of homopolymer **2** was higher than that of homopolymers of styrene and MMA. Therefore, the index values of polymers of styrene and MMA can be increased by copolymerizing these monomers with **1** for optical applications (Table III). When the content of **1** in the copolymer increased, the value of refractive index increased. Applications of copolymers **3** and **4** as well as homopolymer **2** for materials with a higher refractive index are now in progress.

EXPERIMENTAL

Materials: Styrene and MMA were commercial reagents and were purified by distillation. AIBN was purified by recrystallization from methanol. Monomer **1** was prepared according to the literature.[9]

Copolymerization: A typical example (entry 1 in Table I) was as follows. A mixture of monomer **1** (1.25 mmol, 0.165 g), styrene (1.25 mmol, 0.130 g), and AIBN (3mol%, 0.012g) was placed under argon and kept at 80 °C in a sealed tube. After 24 h the reaction mixture was poured into a large amount of n-hexane to precipitate the polymeric material. The copolymer was separated by filtration and dried in vacuo to give 0.206 g (67% yield) of **3**.

Measurement: ^{1}H NMR spectra were recorded on a 250 MHz and 62.8 MHz Bruker AC250T NMR spectrometer. ^{13}C NMR spectra were recorded on a 62.8 MHz Bruker AC250T NMR spectrometer. IR spectra were recorded on a Shimadzu IR-27G spectrometer. UV spectra were recorded on a Shimadzu UV-200 spectrometer. Gel permeation chromatographic (GPC) analysis was performed by using a TOSOH 8010 apparatus with UV detector under the following condition: Gelpack GL-A130 column and chloroform eluent at a flow rate of 1.0 mL/min. Refractive index was measured by using a Shimadzu Abbe refractometer No.53441.

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