Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Radical Polymerization of 2-Methylene-1, 3-dithiane

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

To cite this Article Kobayashi, S. , Kadokawa, J. , Shoda, S. and Uyama, H.(1991) 'Radical Polymerization of 2-Methylene-1, 3-dithiane', Journal of Macromolecular Science, Part A, 28: 1, 1 — 5

To link to this Article: DOI: 10.1080/00222339108054376

URL: http://dx.doi.org/10.1080/00222339108054376

MACROMOLECULAR REPORTS, A28(SUPPL. 1), 1-5 (1991)

RADICAL POLYMERIZATION OF 2-METHYLENE-1,3-DITHIANE

S. Kobayashi,* J. Kadokawa, S. Shoda, & H. Uyama

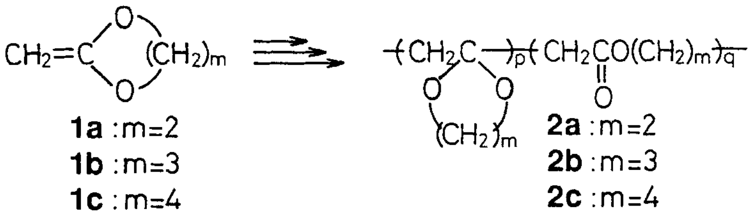
Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba, Sendai 980, Japan

ABSTRACT

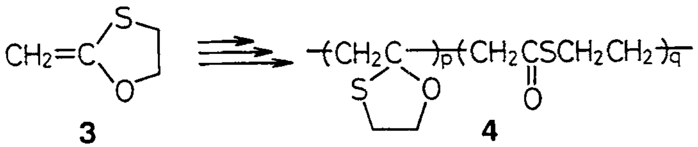
Radical polymerization of 2-methylene-1,3-dithiane, a six-membered cyclic dithioacetal, was carried out to give polymer possessing mainly dithioacetal unit by vinylidene polymerization without ring-opening. The structure was confirmed by ^{1}H, ^{13}C, IR, and UV spectroscopy. On the other hand, a seven-membered cyclic dithioacetal did not polymerize radically.

INTRODUCTION

Some cyclic ketene acetals are known to undergo radical polymerization.[1-3] Among these monomers, 2-methylene-1,3-dioxolane (**1a**) (five-membered) and 2-methylene-1,3-dioxane (**1b**) (six-membered) were radically polymerized to give polymer **2** composed of a vinylidene unit without ring-opening as well as an ester unit with ring-opening.

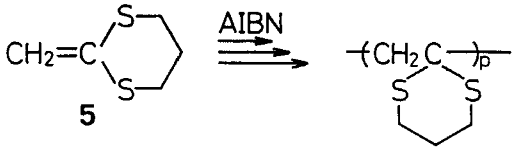


On the other hand, the radical polymerization of 2-methylene-1,3-dioxepane (**1c**) (seven-membered) gave a polyester with complete ring-opening. A sulfur analogue **3** of cyclic ketene acetal **1a** radically polymerized to produce polymer **4** randomly containing a vinylidene unit and a monothioester unit.[4]



3 4

The present paper describes a radical polymerization of 2-methylene-1,3-dithiane (**5**), a six-membered cyclic dithioacetal, to give polymer **6** possessing almost exclusively dithioacetal unit by vinylidene polymerization without ring-opening. To our knowledge, polymerization of **5** has not been reported so far.



5 6

RESULTS AND DISCUSSION

The polymerization of **5** was carried out by using AIBN as initiator at 80°C in benzene or bulk to produce polymer **6**. Polymerization results are given in TABLE 1. The molecular weight of **6** obtained by solution polymerization was relatively low. **6** was soluble in chloroform, benzene, and toluene, but insoluble in n-hexane, methanol, and water.

Polymer **6** has two possible structural units; a dithioacetal unit by vinylidene polymerization and a dithioester unit with ring-opening. FIGURE 1 shows ^{13}C NMR spectra of polymer **6** (entry 1) and 2,4-pentanedione bis(trimethylenedithioacetal) (**7**) as a model compound for vinylidene type polymer. The spectrum of **6** is

TABLE 1
Radical Polymerization of 2-Methylene-1,3-Dithiane (5)[a]

entry	AIBN mol% for **5**	solvent	time (h)	yield[b] (%)	mol. wt.[c]
1	5	benzene	45	39	1500
2	20	benzene	45	52	700
3	2		19	87	
4	10		17	100	
5	30		20	93	1100[d]

[a] Polymerization was carried out at 80 °C by AIBN initiator.
[b] n-Hexane insoluble part. [c] Determined by GPC in chloroform.
[d] Chloroform soluble part.

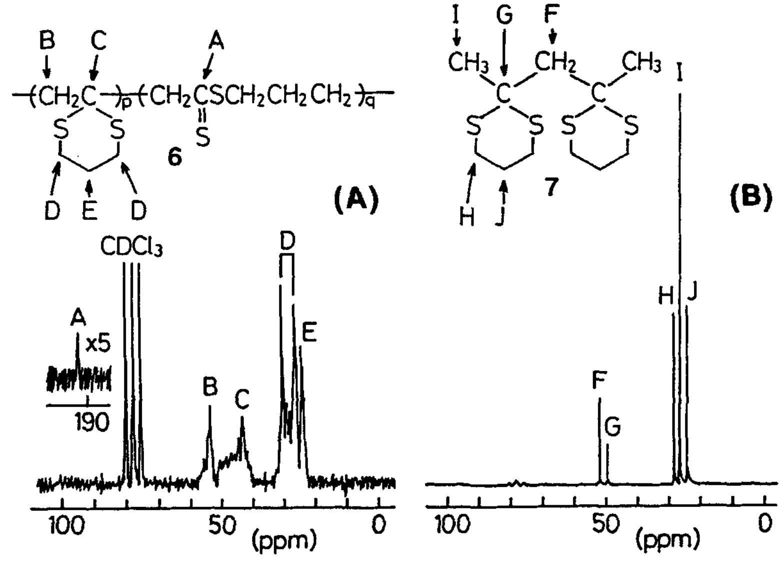
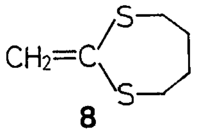


FIGURE 1. ^{13}C NMR spectra($CDCl_3$) of polymer **6** (A) and 2,4-pentanedione bis(trimethylenedithioacetal) (**7**) (B).

very similar to that of **7**. A very small peak at δ 193.4 due to C=S, however, is observed. Therefore, polymer **6** possesses the mixture of dithioacetal unit and dithioester one. Based on the ratio of integrated areas of quaternary carbons of **7** and thiocarbonyl carbon of 3-chloropropyl ditioacetate, a model compound for the dithioester unit, the content of the ring-opened unit calculated from the integrated area of peak A and C was less than 5 %. Other signals' assignment is given in FIGURE 1. IR and UV spectra of **6** did not exhibit the absorptions due to C=S group at 1100 cm^{-1} and 470 nm, respectively, indicating that the content of C=S group is very small, if any.

On the other hand, bulk polymerization of **5** gave a polymer insoluble in all solvents. Elemental analysis data of the polymer agreed well with calculated one and IR spectrum of the polymer was identical with that obtained by solution polymerization. These data support that the structure of the polymer obtained by the bulk polymerization was the same as that by solution polymerization. In the case of the bulk polymerization by using higher initiator concentration (30 mol% for **5**, entry 5), the polymer obtained was partly soluble in chloroform. Therefore, the insoluble polymer may have higher molecular weight.

Relevant to monomer **5**, radical polymerization of 2-methylene-1,3-dithiepane (**8**) was examined. This monomer, however, did not polymerize, probably because of the increased steric hindrance of the seven-membered ring for the propagation.



8

EXPERIMENTAL

Materials: Monomers **5** and **8** were prepared according to the literature.[5] A solvent, benzene, was purified by distillation. An initiator, AIBN, was purified by recrystallization from methanol. All operations were carried out under argon.

Synthesis of 2,4-Pentanedione Bis(trimethylenedithioacetal) (**7**)[6]: To a mixture of 1,3-propanedithiol (4.85 g, 45 mmol) and p-toluenesulfonic acid monohydrate (0.02 g, 0.1 mmol) in 20 mL of benzene was added acetylacetone (2.0 g, 20 mmol) and the reaction mixture was refluxed in the Dean-Stark for 47 h. Then, the mixture was poured into saturated $NaHCO_3$ aqueous solution and extracted with diethyl ether. The organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was subjected to separation by using a silica gel column with n-hexane and diethyl ether to give 3.98 g of **7** (71 % yield): ^1H NMR ($CDCl_3$) δ 1.96 (s, CH_3C, 6H), 1.3-2.2 (m, CCH_2C, 4H), 2.5-3.2 (m, SCH_2, 8H).

Polymerization of **5** (entry 1): A typical run was as follows. A mixture of monomer **5** (0.132 g, 1.0 mmol) and AIBN (0.008 g, 0.05 mmol) was placed in 0.2 mL of benzene under argon and kept at 80 °C for 45 h in a sealed tube. Then, the tube was opened and the reaction mixture was poured into a large amount of n-hexane to precipitate the polymeric materials. The polymer was separated by filtration and dried in vacuo to give 0.051 g (39 % yield) of **6**: ^1H NMR ($CDCl_3$) δ 1.2-2.5 (m, CCH_2C), 2.6-3.2 (m, SCH_2C). Anal. Calcd for $(C_5H_8S_2)_n$: C, 45.45; H, 6.06; S, 48.48. Found: C, 45.77; H, 5.66; S, 47.18.

^1H and ^{13}C NMR spectra were recorded on a JEOL FX-60Q NMR spectrometer with 60 MHz and 15 MHz, respectively. 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 Toyo Soda HLC-802UR with Toyo Soda TSK-GEL columns.

REFERENCES

(1) W. J. Bailey, Polym. J., 17, 85(1985).
(2) W. J. Bailey, Z. Ni, S. R. Wu, J. Polym. Sci., Polym. Chem. Ed., 20, 3021(1982).
(3) T. Endo, M. Okawara, W. J. Bailey, K. Azuma, K. Nate, H. Yokono, J. Polym. Sci., Polym Lett. Ed., 21, 373(1983).

(4) L. Sidney, S. E. Shaffer, W. J. Bailey, Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem., 2, 373(1981).
(5) J. Maijer, P. Vermeer, L. Brandsma, Recl. Trav. Chim. Pays-Bas, 4, 83(1975).
(6) F. Chastrette, M. Hassambay, M. Chastrette, Bull. Soc. Chim. Fr., 601(1976).