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Copolymerization of ethanesultam with 2-methyl-2-oxazoline

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SUMMARY

This paper describes the so-called "No Catalyst Copolymerization" between dioxo-1,1-thiazetidine-1,2(Ethanesultam; ESm) and 2-methyl-2-oxazoline. The copolymerization took place without any added initiator to produce copolymers of MeOZO and ESm. The structure of the copolymer was determined by the IR and NMR spectra, elemental analysis, as well as by the result of an alkaline hydrolysis of the copolymer. The reaction scheme of the copolymerization via zwitterion mechanism (Eq 3-5) was proposed.

INTRODUCTION

Various combinations of copolymerizations between a nucleophilic monomer (M_N) and an electrophilic monomer (M_E) which occur without any added catalyst have been found by us.[1-10] A zwitterion, $^{+}M_N$-M_E^{-} which is the key intermediate of copolymerization, is formed by the interaction between M_N and M_E. In many cases the so-calld alternating copolymers were produced. In the present study, 2-methyl-2-oxazoline (MeOZO) and ethanesultam (ESm) were employed as M_N and M_E, respectively. ESm, a four-memberd ring, which is the isomer of ethylenesulfonamide(ESAm), has been known to give polymer by the ring-opening polymerization with water catalysis.[11)]

RESULTS AND DISCUSSION

Copolymerization and Characterization of Copolymer

An equimolar mixture of MeOZO and ESm (5 mmol each) in 5 ml of benzonitrile was heated at 100 °C under nitrogen. After 54 hr, a polymeric product precipitated from benzonitrile, which was dissolved in DMF solvent, and poured into a large amount of chloroform-benzene system (1 : 1 volume), and purified by repeated reprecipitation. The copolymer was

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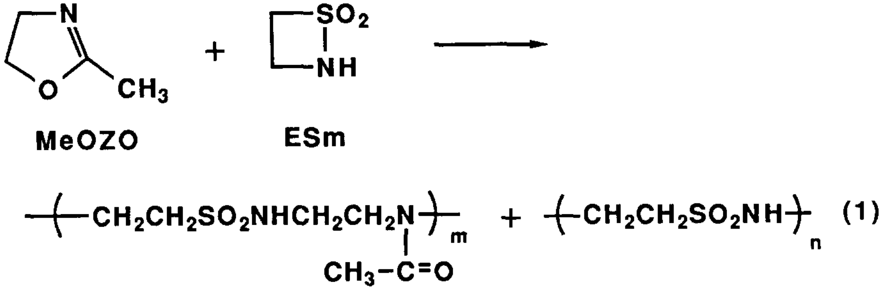
***To whom offprint requests should be sent dried <u>in vacuo</u> to give 0.56 g of a white hygroscopic solid (58% yield), whose molecular weight was measured as 2810 by vapor pressure osmometry in DMF at 55 °C.

The IR spectrum of the copolymer shows absorption bands at 1630 cm^{-1} for the amide carbonyl group, and at 1320 and 1140 cm^{-1} for the sulfonamide group. The NMR spectrum of the copolymer in DMSO-d_6 shows a broad signal at δ4.0-3.0 due to methylene protons of $-CH_2CH_2SO_2NHCH_2CH_2N-$, $-CH_2CH_2SO_2NHCH_2CH_2-SO_2NH-$, and triplet signals at δ2.2, 2.0, and 1.8 due to the acetyl group, and a signal at δ7.3 due to NH. These characteristics of NMR spectrum were the same as those of the MeOZO-ESAm co-oligomer. From the peak ratio of the methyl and methylene signals, MeOZO and ESm units ratio in the copolymer was determined as 1.0 : 1.35. The copolymer composition of MeOZO and ESm was calculated also from an elemental analysis of S (%) content to be 1.00 : 1.26, which is very close to that obtained by NMR analysis.

The copolymerization of MeOZO with ESm was performed under various conditions (Table 1). The composition of copolymers showed a general tendency of ESm in excess. The copolymer are soluble in DMF and DMSO but insoluble in water, methanol, benzene, chloroform and diethyl ether.



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Alkaline hydrolysis of the copolymers was carried out to confirm the structure 1. The completion of hydrolysis was indicated by ^1H NMR spectrum of the reaction mixture. The hydrolysis products are a mixture of the Na salts of β-[(β-aminoethyl) amino] ethanesulfonic acid 2, and of acetic acid, i.e., NMR peaks at δ3.2-2.9 (4H) and 2.9-2.7 (4H) are due to protons of $-NCH_2CH_2N-$ and $-CH_2CH_2S-$, respectively. Methyl protons of the copolymer (δ2.0) were almost completely deuterated. Furthermore, the large broad peak at δ3.3 due to the Na salt of the taurine, $H_2NCH_2CH_2SO_3H$, from the homodiad of

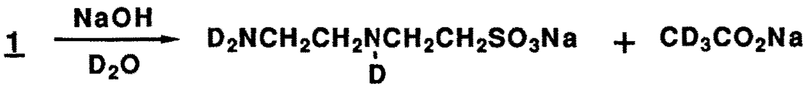
Table 1

Copolymerization of ESm with MeOZO[a]

No	Monomer Feed Ratio (mol) MeOZO / ESm	Solvent	Temp, °C	Time hr	Yield[b] %	%S[c]	Copolymer MeOZO/ESm[d] NMR	from %S	MW[e]
1	1 / 1	PhCN	100	54	58	17.89	1/1.35	1/1.26	2810
2	1 / 1	PhCN	130	30	62	18.53	1/1.50	1/1.39	2770
3	1 / 1	PhCN	80	195	47	19.58	1/1.69	1/1.61	2750
4	1 / 1	CH_3CN	80	248	37	17.23	1/1.24	1/1.12	3720
5	1 / 1	DMF	80	215	56	19.12	1/1.44	1/1.51	-
6	1 / 1	$PhNO_2$	80	210	51	19.49	1/1.70	1/1.59	2920
7	1.4 / 1	PhCN	80	210	52	19.21	1/1.68	1/1.53	2840
8	1 / 1	PhCN + $PhCl_2$ (1/1 volume)	80	253	30	20.83	1/2.03	1/1.88	-

a) The charged MeOZO and ESm were 5.0 mmol except for No.7 in 5.0 ml of solvent.
b) (Copolymer(g)/Total feed monomer(g)) x 100.
c) The calculated S(%) = 16.68 for the 1 / 1 composition.
d) The MeOZO/ESm ratio of the copolymer was determined by NMR spectra and the elemental analysis (%S), respectively.
e) Determined by VPO in DMF at 55 °C.

the ethanesultam unit is seen. The pattern of these signals was almost the same as that of the hydrolysis product of MeOZO-ESAm co-oligomer.9) Thus, the structure of MeOZO-ESm copolymer has been confirmed as 1.



$$\underline{1} \xrightarrow[D_2O]{NaOH} D_2NCH_2CH_2\underset{D}{N}CH_2CH_2SO_3Na + CD_3CO_2Na \qquad (2)$$

Na salt of 2

Copolymerization Mechanism

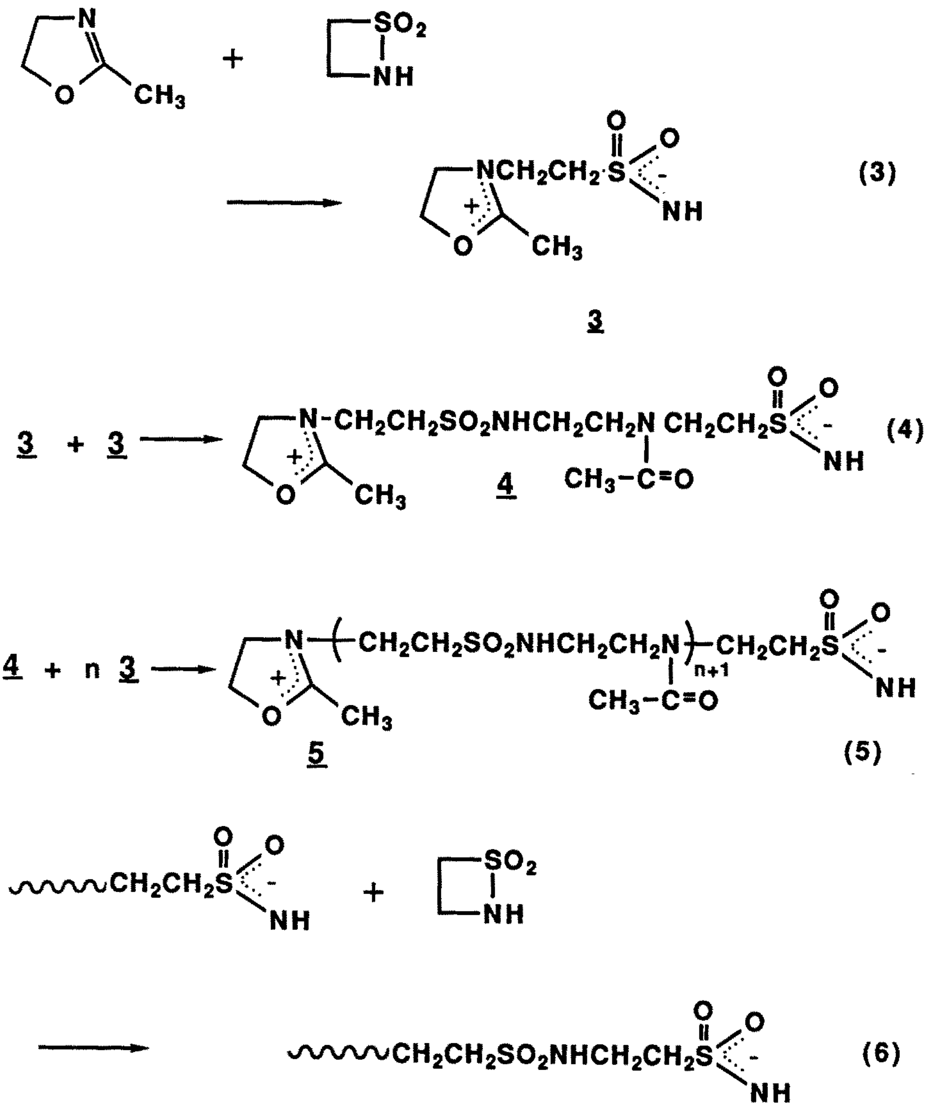
On the basis of the above data, a zwitterion mechanism on the next page is proposed to explain the present copolymerization. The course of the MeOZO-ESm copolymerization is schematically formulated in Eqs 3-6.

The zwitterion 3 is first formed from ESm and MeOZO (Eq 3). Then, the reaction of 2 mol of zwitterion 3 takes place, in which the sulfonamide group of one zwitterion behaves as a nucleophile to attack the O-methylene carbon atom of the oxazolinium ring of another zwitterion to cause the ring-opening isomerization of the oxazolinium ring (Eq 4). A dimeric zwitterion of 4 is thus formed, which in turn reacts successively with 3 (Eq 5) in the same way as in the reaction of two molecules of 3. The propagation consists of the successive linkings of zwitterion molecules to one of ionic ends of the macrozwitterion 5 through the interaction between the sulfonamide anion group and oxazolinium ring. In the present copolymerization, the sulfonamide anion of 3, 4, and 5, is an ambident anion of oxygen and nitrogen. ESm gives a sulfonamide unit in the copolymer 1 via the regiospecific reaction at the nitrogen atom of the ambident anion. In addition to the above scheme, the homopropagation of ESm takes place to disturb the 1 : 1 alternating arrangement of the two monomeric units (Eq 6).

EXPERIMENTAL

Materials

ESm was synthesized according to the procedure given by Le Berre and Petit12) by the reaction of β-aminoethanesulfonic acid with phosphorus oxychloride, followed by cyclization with anhydrous ammonia. It was recrystallized repeatedly in benzene : white scaly crystal, mp 49 °C (lit. 53 °C).12)



Anal. Calcd for $C_2H_5NO_2S$: C, 22.42; H, 4.70; N, 13.08; S, 29.93. Found: C, 22.65; H, 5.00; N, 12.82; S, 29.88. ^{1}H NMR ($CDCl_3$): δ3.2-3.6 (m, CH_2S-, 2H), 4.2-4.5 (t, CH_2N-, 2H), 5.9 (s, NH, 1H). IR (KBr) : 1300 and 1150 cm^{-1} (SO_2).

MeOZO was purchased from Aldrich Chemical Co. and purified by distillation, bp 110 °C. All solvents were purified by distillation in usual manners.

Polymerization Procedure

To 5 ml of solvent, 5.0 mmol each of MeOZO and ESm were added at room temperature and the reaction mixture was kept at a desired temperature. After the reaction, the polymeric product precipitated from the reaction solvent, which was dissolved in DMF solvent, and poured into a large amount of chloroform-benzene system, and purified by repeated reprecipitation. A white hygroscopic material was obtained after drying *in vacuo*, and analyzed by IR, NMR, elemental analysis and alkaline hydrolysis experiment.

Alkaline Hydrolysis of Copolymer

To 50 mg of copolymer was added 0.5 ml of a 15% NaOH aqueous solution of D_2O. The mixture was kept at 90-95 °C for 20 hr. The reaction product was directly subjected to NMR measurement.

Molecular Weight Determination

The molecular weight of the copolymer was measured by vapor pressure osmometry (Hitachi Perkin-Elmer Model 115) in DMF at 55 °C.

REFERENCES

1. T. Saegusa, H. Ikeda, and H. Fujii, Macromolecules, **5**, 354 (1972).
2. T. Saegusa, S. Kobayashi, and Y. Kimura, Macromolecules, **7**, 1 (1974).
3. T. Saegusa, S. Kobayashi, and Y. Kimura, Macromolecules, **7**, 139 (1974).
4. T. Saegusa, Y. Kimura, K. Sano, and S. Kobayashi, Macromolecules, **7**, 546 (1974).
5. T. Saegusa, Y. Kimura, S. Sawada, and S. Kobayashi, Macromolecules, **7**, 956 (1974).
6. T. Saegusa, S. Kobayashi, and Y. Kimura, Macromolecules, **8**, 374 (1975).
7. T. Saegusa, S. Kobayashi, Y. Kimura, and H. Ikeda, J. Macromol. Sci., Chem., **9**, 641 (1975).
8. T. Saegusa, S. Kobayashi, and J. Furukawa, Macromolecules, **8**, 703 (1975).
9. T. Saegusa, S. Kobayashi, and J. Furukawa, Macromolecules, **9**, 728 (1976).
10. T. Saegusa, Y. Kimura, N. Ishikawa, and S. Kobayashi, Macromolecules, **9**, 724 (1976).
11. Y. Imai, H. Hirukawa, J. Polym. Sci., Polym. Lett. Ed., **11**, 271 (1973).
12. A. Le. Rerre, and J. Petit, Tetrahedron Lett., 213 (1972).

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