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# Polyaddition between 2-alkenyl-2-oxazoline and N-acetyl-L-cysteine

## Synthesis of optically active poly(amide-thioether-ester)

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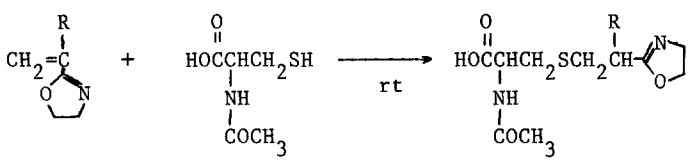
Summary

Polyaddition between 2-isopropenyl(or 2-vinyl)-2-oxazoline and N-acetyl-L-cysteine gave an optically active poly(amide-thioether-ester). This polymerization proceeds via a conjugate addition followed by the subsequent ring-opening addition reaction. No racemization of the original chiral center was observed during the polymerization. However, the asymmetric induction to the prochiral center of isopropenyl-2-oxazoline hardly occurred.

Introduction

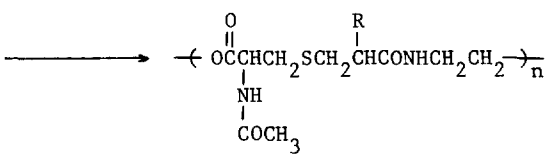
In the former report, a new polyaddition reaction between 2-alkenyl cyclic imino ether and mercaptocarboxylic acid was described (1). The present paper is concerned with the application of the above polyaddition to the synthesis of an optically active poly(amide-thioether-ester). For that purpose, N-acetyl-L-cysteine 2 was used as a mercaptocarboxylic acid component to be polymerized with 2-isopropenyl- and 2-vinyl-2-oxazoline (1a and 1b) repectively (scheme 1).

Scheme 1




1a: R=$CH_3$ 2 3a: R=$CH_3$

1b: R=H 3b: R=H



4a: R=$CH_3$

4b: R=H

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A Michael type adduct 3 is the intermediate of this polymerization. In the Michael type addition, some examples of an asymmetric induction by an chiral enolate have been known (2). It has been also reported that polyaddition between dithiol and dimethacrylate in the presence of an optically active catalyst gave an slightly optically active polymer (3). So, an asymmetric induction was expected in the production of 3 when 1a (not 1b), which has a prochiral center, was the reaction partner of 2, however, the asymmetric induction was not observed in this study.

## Experimental

Materials 2-isopropenyl- and 2-vinyl-2-oxazoline were prepared according to reported methods (4). N-acetyl-L-cysteine (Aldrich Chem. Co.) was used without purification. DMF for the reaction solvent was dried with $CaH_2$ and distilled under reduced pressure.

Polymerization According to a similar procedure to that described in the preceding paper (1), 2-isopropenyl-2-oxazoline 1a (618 mg, 5.4 mmol) was reacted with N-acetyl-L-cysteine 2 (908 mg, 5.4 mmol) in DMF (4.58 g) to give a white powdery polymer. Under the same conditions, 2-vinyl-2-oxazoline 1b was also polymerized.

Measurment Molecular weight of the polymer product was estimated by GPC using polystyrene standards at 50 °C; eluent DMF containing LiBr (0.2 wt%), column TSK-GEL® G4000 (TOYOSODA Co.). Optical rotation of the polymer was measured in DMF (C=0.05 g/10 ml).

Spectroscopic data (3a) $^1$H NMR (400 MHz, DMSO-$d_6$) δ 1.20 (d, J=6.3 Hz, 3H, $CHCH_3$), 1.92 (S, O=$CCH_3$), 2.62 (m, 2H, $CH_2CHC$=N), 2.71 (m, 2H, HNCH$CH_2$), 2.90 (m, 1H, $CHCH_3$), 3.75 (t, J=9.4 Hz, 2H, =$NCH_2$), 4.21 (t, J=9.4 Hz, 2H, $OCH_2$), 4.46 (m, 1H, NHCH) 8.16 (d, J=7.0 Hz, 1H, NH), 12.3 (b, 1H, $CO_2$H); $^{13}$C NMR 22.6 MHz DMSO-$d_6$/$CDCl_3$=2/1 (v/v)) δ 17.07 ($CHCH_3$), 22.42 (C(=O)$CH_3$), 33.66 ($CHCH_3$ and NHCH$CH_2$), 35.91 ($CH_2CHC$=N), 52.13 (=$NCH_2$), 53.80 (NHCH), 67.01 ($OCH_2$), 169.41 (N=C-O), 169.63 (NHC=O), 172.33 ($CO_2$H). (3b) $^1$H NMR (60 MHz, DMSO-$d_6$) δ 2.07 (s, $CH_3$), 2.4-3.2 (m, 6H, $CH_2SCH_2CH_2$), 3.7-4.5 (m, 4H, $OCH_2CH_2$N=), 4.75 (m, 1H, CH), 7.90 (b, 1H, NH), 13.2 (b, 1H, $CO_2$); $^{13}$C NMR (22.6 MHz, DMSO-$d_6$) δ 22.55 ($CH_3$), 27.48 ($CH_2CH_2C$=N), 28.22 ($CH_2C$=N), 33.52 (NHCH$CH_2$), 52.35 (=$NCH_2$), 53.25 (CH), 67.64 ($OCH_2$), 167.33 (N=C-O), 170.57 (NHC=O), 172.59 ($CO_2$H). (4a) $^1$H NMR (60 MHz, DMSO-$d_6$) δ 1.13 (b, 3H, $CHCH_3$), 1.92 (s, 3H, O=$CCH_3$), 2.4-3.1 (m, 5H, $CH_2SCH_2CHCH_3$), 3.39 (b, 2H, $NCH_2$), 4.11 (b, 2H, $OCH_2$), 4.40 (b, 1H, NCH), 7.9-8.2 (m, 2H, NH); $^{13}$C NMR (22.6 MHz, DMSO-$d_6$) δ 17.43 ($CHCH_3$), 22.38 (O=C$CH_3$), 33.39 (NCHC$H_2$), 35.69 ($CH_2CHCH_3$), 37.72 ($NCH_2$), 40.41 ($CHCH_3$), 52.31 (NCHC=O), 63.3 ($OCH_2$), 169.91 (O=$CCH_2$), 170.63 (O=CO), 174.80 (C(=O)$NHCH_2$); IR (KBr, $cm^{-1}$) 3280, 3075, 2950, 2925, 1740, 1658, 1545, 1440, 1385, 1210, 1180, 1125, 1040. (4b) $^1$H NMR (60 HMz, DMSO-$d_6$) δ 2.0 (s, 3H, $CH_3$), 2.4-3.1 (m, 6H, $CH_2SCH_2CH_2$), 3.3-3.7 (b, 2H, $NCH_2$), 4.0-4.8 (b, 3H, $CH_2OC$(=O)CH), 7.4-8.3 (b, 2H, NH); $^{13}$C NMR (22.6 MHz, DMSO-$d_6$) δ 22.29 ($CH_3$), 27.55 (S$CH_2CH_2$), 33.75 ($CHCH_2S$), 35.54 ($CH_2C$=O), 37.61 ($NCH_2$), 52.21 (O=CCHN), 63.32 ($OCH_2$), 169.67 (OC=O and O=$CCH_3$), 170.79 (O=CNHCH$_2$).

## Results and Discussion

The polyaddition described here consists of two different elemental addition reactions. At the first stage, the thiol group of 2 adds to the olefinic double bond of 1a (or 1b) below room temperature to produce the adduct 3a (or 3b) quantitatively. To confirm the structure of 3a and 3b,

Table 1. Polymerization of 1 with N-Acetyl-L-Cysteine 2 in DMF.[a)]

| No. | 1 | Temp. (°C) | Time (hr) | Yield (wt%)[b)] | $M_W$[c)] | $M_W/M_N$[c)] | $[\alpha]_D^{20}$ |
|---|---|---|---|---|---|---|---|
| 1 | 1a | 50 | 48 | 88 | 7200 | 1.33 | -18.3 |
| 2 | 1b | 50 | 48 | 91 | 6300 | 1.64 | -18.5 |
| 3 | 1a | 100 | 24 | 96 | 13800 | 1.77 | -21.1 |
| 4 | 1b | 100 | 24 | 94 | 8260 | 1.59 | -22.8 |

a) Solvent/Monomers = 3/1 (wt/wt). b) Insolble polymer in ether.
c) GPC (based on PSt standard), eluent: DMF + 0.2 wt% LiBr.
d) c = 0.05 g/10 ml DMF

they were prepared in DMSO-$d_6$ and subjected to the $^1H$ and $^{13}C$ NMR spectroscopic analysis in situ (see Experimental Section). Then, the adduct 3 was heated to be polymerized (Table 1). The product polymers 4a and 4b, whose structures were suported by their $^1H$, $^{13}C$ NMR and IR spectra (see Experimental Section), were optically active ($[\alpha]_D^{20}$ = -18.3~-22.8). When the polymerization temperature was raised from 50 to 100 °C, the MW and the absolute value of $[\alpha]_D^{20}$ were increased in the both cases of 4a and 4b. Therefore, it is assumed that the racemization of the chiral center due to N-acetyl-L-cysteine did not take place. However, the very small difference about $[\alpha]_D^{20}$ value between 4a and 4b, which were prepared at either temperature (50 and 100 °C), indicate that an asymmetric induction at the production 3a scarcely occurred.

References

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3. S. Inoue, S. Ohashi, A. Tabata, and T. Tsuruta, Makromol. Chem. 112, 66 (1986).
4. see ref. 10 in ref. 1.

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