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Polyaddition between 2-alkenyl cyclic imino ether and mercaptocarboxylic acid

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Summary

A new polyaddition reaction between 2-alkenyl cyclic imino ether 1 and mercaptocarboxylic acid 2 was discovered. This polyaddition consists of two steps. The first reaction is the addition of a mercapto group of 2 to an activated carbon-carbon double bond of 1, which takes place at room temperature to produce the adduct 3. The second reaction is an intermolecular reaction between the carboxy group and the cyclic imino ether group with ring-opening which produces poly(amide-thioether-ester) 4.

Introduction

2-Alkenyl cyclic imino ether 1 has two polymerizable functional groups, i.e., alkenyl and cyclic imino ether groups. Cationic ring-opening polymerization of the cyclic imino ether ring (1), and radical (1, 2) or anionic (3) polymerization of the alkenyl group have been reported. Recently, the spontaneous, radical, and base-catalyzed polymerizations of N-alkylated (or protonated) 2-alkenyl cyclic imino ether salts has been developed in our laboratory (4). On the other hand, 2-oxazoline ring is known to react with some functional groups such as carboxylic acid and thiol (5). These reactions have been applied to polymer synthesis, i.e., polyaddition between bis(2-oxazoline) and dicarboxylic acid (or dithol)(6, 7), and thermal polymerization of 2-mercaptoalkyl-2-oxazoline (8). In addition, the polymerization of 2-isopropenyl-2-oxazoline with dithiol has been reported very recently (9).

The present paper (10) describes a new polyaddition between 2-alkenyl cyclic imino ether and mercaptocarboxylic acid. As the first component, 2-isopropenyl-2-oxazoline 1a, 2-isopropenyl-5,6-dihydro-4H-1,3-oxazine 1b, and 2-vinyl-2-oxazoline 1c were employed, and as the second component thiolactic acid 2a and thioglycolic acid 2b were used. This polymerization consists of two different elemental reactions, i.e., the conjugate addition of the mercapto group of 2 to the olefinic double bond of 1 and the subsequent intermolecular reaction of the adduct involving the ring-opening of the cyclic imino ehter group by the carboxy group to produce poly(amide-thioether-ester) 4 (scheme 1).

Experimental

Materials 2-Alkenyl cyclic imino ethers 1a, 1b, and 1c were prepared according to reported methods (11). Methyl ester of 3a (and 3c) was synthesized by stirring of methyl thiolactate with 1a (and 1b) in $CHCl_3$ at room temperature for 2 hr. All other reagents and solvents were purified and dried by conventional techniques.

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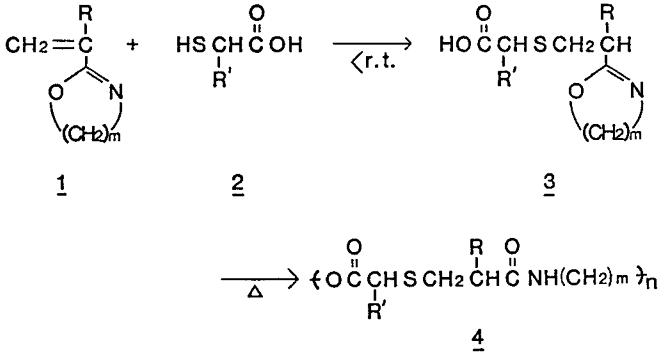
Scheme 1



1a; R=CH_3, m=2
1b; R=CH_3, m=3
1c; R=H , m=2

2a; R'=CH_3
2b; R'=H

3a (4a); R=CH_3, R'=CH_3, m=2
3b (4b); R=CH_3, R'=H , m=2
3c (4c); R=CH_3, R'=CH_3, m=3
3d (4d); R=H , R'=CH_3, m=2
3e (4e); R=H , R'=H , m=2

Polymerization A typical procedure was as follows. 2-Isopropenyl-2-oxazoline 1a (0.900 g, 8.10 mmol) was added slowly to thiolactic acid 2a (0.860 g, 8.10 mmol) in 1.2 ml of dry $CHCl_3$ with vigorous stirring at 0 °C under nitrogen atmosphere. After 1 hr at room temperature, the solution was heated at 100 °C for 40 hr. The reaction mixture was diluted with 15 ml of $CHCl_3$, which was then poured into 200 ml of diethyl ether. The precipitated polymer was filtrated and dried *in vacuo* (1.74 g, 99%).

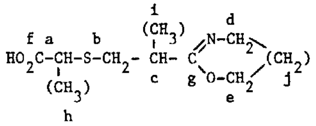
The bulk polymerization was carried out after evaporation of $CHCl_3$ *in vacuo* before heating the reaction mixture.

Measurements Molecular weight of the polymer was estimated by GPC using polystyrene standards; eluent (column) was $CHCl_3$ ($Shodex_R$ A803 at ambient temperature) for 4a and 4c, and DMF containing 0.2 wt % of LiBr ($TSK\text{-}GEL_R$ G4000 at 50 °C) for 4b.

Results and Discussion

Conjugate addition of 2 to 1 The reaction of 2-isopropenyl-2-oxazoline 1a with thiolactic acid 2a in $CDCl_3$ was followed by ^1H NMR spectroscopy. The growth of the signals related to a thioether group and the concurrent decrease of the both signals assigned to the isopropenyl and the mercapto groups were observed. The addition reaction completed within 1 hr at room temperature to produce the adduct 3a quantitatively. ^1H and ^{13}C NMR (*in situ*) data of all the adducts 3 are given in Table 1. In ^{13}C NMR of 3a and 3c, some signals consist of two sets because they are the mixtures of two diastereomers. The carbon atom of the imino group of 3a gives two signals at 171.97 and 172.06 ppm, which are at a 3.41 ppm lower field and at a 7.84 (and 7.74) ppm higher field as compared with the corresponding signals of methyl ester of 3a (168.56 and 168.65 ppm) and its protonated salt (179.89 ppm) with trifluoromethanesulfonic acid respectively. These findings are taken to indicate that 3a is not completely in the zwitter-ionic form but in the form where the nitrogen atom of the oxazoline ring

Table 1. ^{1}H and ^{13}C NMR data of 3[1]



		a	b	c	d	e	f	g	h	i	j
3a[2]	^{1}H [5]	3.39(m)	2.84(m)	2.72(m)	3.88(t, J=9.2)	4.35(t, J=9.2)	14.54(b)	—	1.403(d, J=7.21)	1.274(d, J=6.84)	—
				3.03(m)					1.396(d, J=7.20)	1.268(d, J=6.22)	—
	^{13}C	41.21	34.69	33.66	52.58	67.91	175.12	171.97	17.26	17.03	
		41.48		33.84				172.06			
3b[3]	1H [5]	3.25(s)	2.94(m)	2.78(m)	3.90(t, J=9.4)	4.36(t, J=9.4)	14.8(b)	—	—	1.29(J=6.83)	—
	^{13}C	35.30	34.31	33.54	52.20	68.11	171.66	171.72	—	16.96	—
3c[2]	^{1}H	3.43	2.82(m)	2.82(m)	3.48(t, J=6.0)	4.28(t, J=6.0)	14.51(b)	—	1.41(d, J=7.2)	1.22(d, J=6.0)	1.97(m)
	^{13}C	42.61	34.47	39.82	40.09	66.25	177.00	168.10	17.88	17.39	20.72
		43.32	35.23	40.09				168.51			
3d[4]	^{1}H	3.46(q, J=7.2)	2.64	2.84(m)	3.60	4.30(m)	15.87(b)	—	1.41(d, J=7.2)	—	—
	^{13}C	40.34	26.11	27.32	52.62	66.56	173.63	166.03	16.39	—	—
3e[3]	^{1}H	3.25(s)	2.43	2.96(m)	3.40	4.40(m)	12.21	—	—	—	—

[1] ^{1}H and ^{13}C NMR spectra were recorded on 60 MHz (for ^{1}H) and 22.6 MHz (for ^{13}C) spectrometer respectively unless otherwise note. A chemical shift and a coupling constant (J) are shown in value and Hz respectively. [2] In $CDCl_3$. [3] In DMSO-d_6/$CDCl_3$ = 2/1 (v/v). [4] In DMSO-d_6. [5] 400 MHz

Table 2. Polymerization of the Adducts 3 at 100 °C

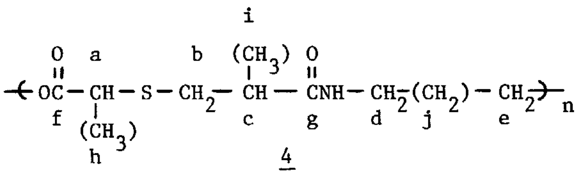
No.	3	Solv.$^{a)}$	hr	Yield$^{b)}$	$M_W$$^{c)}$	$M_W/M_n$$^{c)}$
1$^{d)}$	3a	none	1	67$^{e)}$	3350$^{e)}$	1.54
2	"	$CHCl_3$	40	99	6750	1.65
3	"	DMF	40	95	8850$^{g)}$	2.28
4	3b	"	48	95	5400	—
5	3c	none	1	—	10000	4.26
6$^{d)}$	"	"	3	49$^{e)}$	14000$^{e)}$	2.24
7	"	$CHCl_3$	40	91	6700	1.84
8$^{d)}$	3d	DMF	7	76$^{f)}$	—	—
9$^{d)}$	3e	"	24	79$^{f)}$	—	—

a) Solvent/Monomers=1/1 (wt/wt). b) Insoluble polymer in ether (wt%). c) GPC (based on PSt standard). d) Partial gelation. e) Soluble polymer in $CHCl_3$. f) Soluble polymer in the mixture solvent; $CHCl_3$/MeOH=1/1 (v/v). g) M_n evaluated by VPO ($CHCl_3$, 40°C) is 5200.

and the carboxy group of 3a interact with each other (hydrogen bond). A similar phenomenon was observed also in the case of 3c with 1,3-oxazine ring; 168.10 and 168.51 ppm for 3c, 160.03 ppm (another signal was not observed) for methyl ester of 3c, and 177.24 ppm (another signal was not observed) for the protonated salt of methyl ester of 3c. This interaction of the imino ether group with the carboxy group is taken to enhance the electron-withdrawing character of the imino ether group to facilitate the conjugate addition reaction.

Polymerization of 3 The adduct 3 produced in situ was heated directly at 100 °C without purification (Table 2). Solution polymerization (in $CHCl_3$ or DMF) of 3a - 3c gave the soluble polymers in good yields whereas the bulk polymerization of 3a and 3c and also the solution polymerization (DMF) of 3d and 3e resulted in partial gelation. The gelated product was extracted with a mixed solvent ($CHCl_3$/MeOH = 1/1 (v/v)) to isolate the soluble part in 40-80%. The obtained polymers were colorless or yellowish solids, which were soluble in DMF, DMSO, and the mixed solvent ($CHCl_3$/MeOH = 1/1 (v/v)), and insoluble in ether, CH_3CN, acetone, and $CHCl_3$ (however, 4a and 4c were soluble in $CHCl_3$). The spectroscopic data are shown in Table 3. The structure of polymer was independent on the polymerization conditions. Any structural difference between the polymer from the solution polymerization and the soluble polymer from the bulk polymerization was not observed in the spectroscopic analysis. The IR spectra of all polymers showed absorption bands corresponding to ν C=O of ester groups (1720-1740 cm^{-1}), and ν C=O (1640-1650 cm^{-1}) and δ N-H (1540-1545 cm^{-1}) of secondary amide groups. ^{13}C NMR spectra also support the structure of poly(amide-thioether-ester). The spectrum of 4a is slightly complicated due to the diastereomeric units. The results of elemental analsis were quite satisfactory.

Table 3. Spectroscopic data of $\underline{4}^{1)}$



$$-\!\!\left(\overset{O}{\overset{\|}{O C}}_{f}-\underset{\underset{h}{(CH_3)}}{\overset{a}{CH}}-S-\overset{b}{CH_2}-\underset{c}{\overset{\overset{i}{(CH_3)}}{CH}}-\underset{g}{\overset{O}{\overset{\|}{C}}}NH-\underset{d}{CH_2}-\underset{j}{(CH_2)}-\underset{e}{CH_2}\right)\!\!-_{n}$$

$\underline{4}$

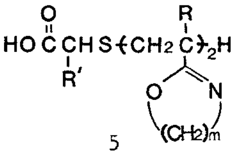
		a	b	c	d	e	f	g	h	i	j
4a	^{1}H 2)	3.52	2.50	3.00(m)	3.52	4.25	—	7.81	1.41(d, J=7.2)	1.22(d, J=6.0)	—
	^{13}C 2)	40.70 41.55	34.46 35.56	41.15	38.87	63.96	173.01	175.55	17.84 18.21	17.05	—
	IR	3300, 3090, 2970, 2940, 1726, 1650, 1543, 1457, 1390, 1327, 1240, 1165, 1072 etc.									
4b	^{1}H 3)	3.26	2.50	3.00(m)	3.58	4.27	—	7.8	—	1.25(d, J=6.0)	—
	^{13}C 4)	35.60	33.20	40.14	37.80	63.33	170.60	175.35	—	17.08	—
	IR	3300, 3075, 2960, 2930, 1723, 1650, 1542, 1452, 1420, 1375, 1280, 1145, 1030 etc.									
4c	^{1}H 2)	3.39	2.56	2.97(m)	3.48	4.21	—	7.36	1.41(d, J=7.2)	1.23(d, J=6.0)	1.92
	^{13}C 2)	40.98 41.21	34.92	41.07	36.08	62.51	173.14	175.20	17.66 17.79	17.02	28.40
	IR	3280, 3070, 2970, 2925, 1723, 1640, 1540, 1448, 1373, 1320, 1237, 1160, 1065 etc.									
4d	^{1}H 3)	3.53(m)	2.86	2.62	3.53(m)	4.20	—	8.01	1.42(d, J=7.2)	—	—
	^{13}C 5)	41.13	27.26	36.23	38.88	64.15	173.82	172.92	17.13	—	—
	IR	3300, 3050, 2970, 2940, 1725, 1643, 1542, 1452, 1375, 1320, 1240, 1160, 1068 etc.									
4e	^{1}H 3)	3.25	2.40	2.85(m)	3.34	4.12	—	8.04	—	—	—
	^{13}C 4)	35.67	28.25	33.30	28.25	63.37	170.0	171.75	—	—	—
	IR	3300, 3080, 2970, 2940, 1732, 1645, 1545, 1418, 1275, 1145, 1038 etc.									

1) ^{1}H and ^{13}C NMR spectra were recorded on 60 MHz (for ^{1}H) and 22.6 MHz (for ^{13}C) spectrometer respectively. A chemical shift and a coupling constant (J) are shown in value and Hz respectively. A chemical shift in ^{1}H NMR spectra is represented by the shift value of the peak top or the center of the peaks. IR spectra were measured by KBr technique and representative absorbance bands are shown in cm^{-1}.

2) In $CDCl_3$ 3) In DMSO-d_6 4) In $CDCl_3/CD_3OD$ = 2/1 (v/v) 5) In $CDCl_3/CD_3OD$ = 1/2 (v/v)

In GPC, all polymers exhibited a single peak, from which M_W and M_W/M_N were evaluated. These values of the polymers obtained by the bulk polymerization were higher than those from the solution polymerization. Morever, the solution polymerization in DMF yielded the polymer with higher values of M_W as well as M_W/M_N than the respective values of that in $CHCl_3$ after the same reaction time.

An insoluble portion in several runs (No 1, 6, 8, and 9 on Table2) was presumably produced by cross-linking reaction, for which the following possibilities are conceived, i.e., 1) the protonated oxazoline ring is opened by the nucleophilic attack of another oxazoline ring un-protonated or of amide group of product polymer to give the resultant polymer a branch (12). A cross-linking reaction occurs when the polymer chain having branches is cleaved at S-C bond to give a thiol group and a methacryl (or acryl) amide group (retro Michael), which subsequently recombine with another molecules. These groups can be also formed by the reverse reaction of the adduct 3 to 1 and 2 which participate in the polymerization. 2) Simultaneously with the production of 3 from 1 and 2, the undetectable amount of a bis(oxazoline) such as 5 happen to be formed. 5 can act as a cross-linking agent. These side reactions for the cross-linking seems to be favored by the higher concentration, whose extremity is the bulk polymerization.



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The faster gelation of 3a than 3c at bulk polymerization (No 1 and 5 on Table 1) was probably due to the higher ring-opening activity of an oxazolinium ring than an oxazinium ring. Even at the solution polymerization, 3d and 3e respectively gave an insoluble portion (No. 8 and 9 on Table 2). This is presumably due to the fact that 3d and 3e have no methyl group, which sterically hinder the above-mentioned side reactions for the cross-linking, at the α-position of the iminoether group.

The effect of temperature on the solution polymerization of 3a in $CHCl_3$ was investigated (Figure 1). In the temperature range below 100 °C,

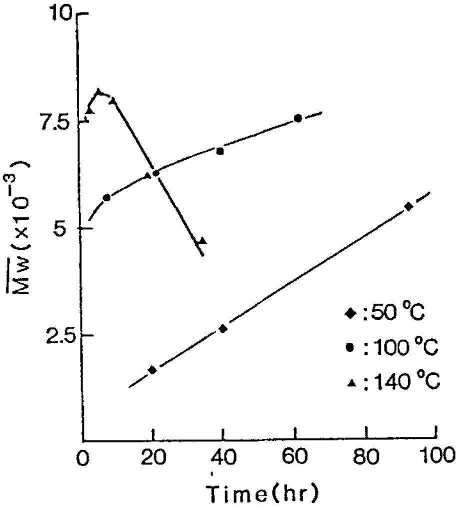

Figure 1. Time-MW curves in the polymerization of 3a which is the adduct of 1a with 2a in $CHCl_3$, solvent/monomers = 1/1(wt/wt).

the molecular weight of the resultant polymer increased with the reaction temperature and the longer polymerization time. However, at 140 °C, the molecular weight of the polymer showed the maximum value after 5 hr, and the further heating induced lowering of the molecular weight and increasing of M_W/M_N. This means that the degradation (probably S-C bond scission) of the polymer occurred at 140 °C.

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