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Reactivity of *N*-alkylated cyclic imino ether salts having vinyl group

5. Graft copolymerization of 2-oxazolines onto copolymer of 2-isopropenyl-3-methyl-2-oxazolinium tetrafluoroborate with acrylate

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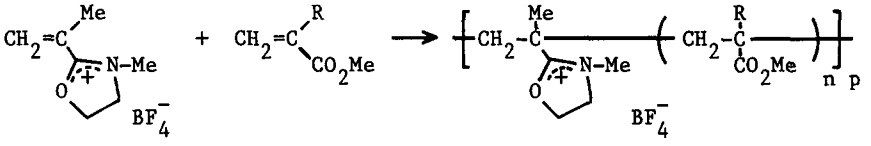
Summary

Two copolymers of 2-isopropenyl-2-oxazolinium tetrafluoroborate with methyl methacrylate and with methyl acrylate were prepared, from which the polymerization of 2-oxazolines (2-methyl and 2-t-butyl) was initiated to prepare graft copolymers.

Introduction

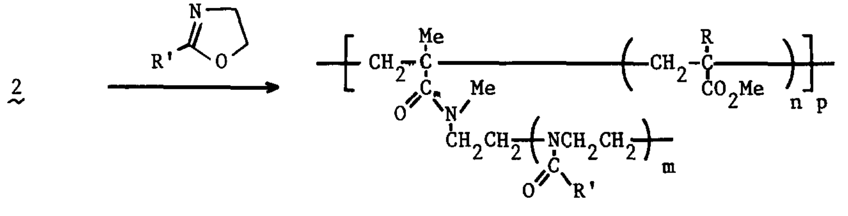
A previous paper of us reported the radical polymerization and copolymerization of N-methyl salt of 2-isopropenyl-2-oxazoline (1). By these polymerization and copolymerization were prepared the polymers having oxazolinium pendant groups which are considered to have potentialities of derivatization. In the present study, the copolymers of 2-isopropenyl-3-methyl-2-oxazolinium tetrafluoroborate (1) with methyl methacrylate (MMA) and with methyl acrylate (MA), shown by 2a and 2b, respectively, were prepared (Eq. 1), from which the polymerization of 2-oxazolines was initiated to prepare the corresponding graft copolymers 5a and 5b having poly[(N-acyl)iminoethylene] branches (Eq. 2).



(Eq.1)

1

2a, R=Me
2b, R=H



(Eq.2)

4a, R'=Me
4b, R'=t-Bu

5a, R=R'=Me
5b, R=H, R'=Me
5c, R=H, R'=t-Bu

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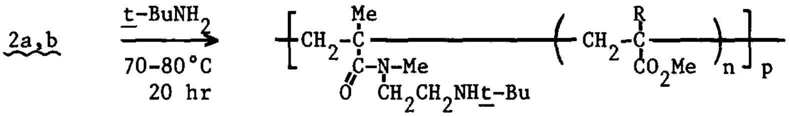
Experimental

Materials. 2-Methyl- (4a) and 2-*t*-butyl-2-oxazoline (4b) were prepared as before (2). 1 was prepared by *N*-alkylation of 2-isopropenyl-2-oxazoline with trimethyloxonium tetrafluoroborate (1).

Preparation of copolymers 2. Two samples of each of the copolymers 2a and 2b were prepared by the radical copolymerization of 1 with MMA and MA, respectively (Table 1). The products isolated were all yellow solid materials whose viscosities in CH_3CN containing 2 wt% of NaI were in a range of 0.1-0.3. Their unit ratios (oxazolinium unit/acrylate unit) were dependent upon the feed ratio of two monomers, which were measured by ^1H NMR spectra as 0.2 (2a-1), 0.41 (2a-2), 0.085 (2b-1), and 0.17 (2b-2), respectively. For further characterization, these copolymers were reacted with *t*-butylamine to convert the oxazolinium ring to more stable aminoethylamide group. The reaction was carried out by the same method as before (3).



3a, R=Me
3b, R=H

The products, recovered in over 80% yields, was characterized as 3 (the footnotes of Table 1). GPC analysis was made also with 3. These data provide important information concerning the molecular weight and the molecular weight distribution of the parent samples of 2.

Graft copolymerization. A typical run was as follows. In a test tube equipped with a three way stop-cock and a magnetic stirrer, 0.447 g of 2a-2 (corresponding to 0.975 mmol of the oxazolinium unit), 0.828 g of an oxazoline monomer 4a (9.75 mmol), and 20 ml of DMF were mixed under nitrogen. The tube was sealed and kept at 80 °C for 10 hrs with stirring. Then, the reaction mixture was poured into 200 ml of a mixture (1:2-/vol.) of CH_2Cl_2 with Et_2O to precipitate the product. The crude product was treated with 10 mequiv. of an anion exchange resin (Amberlite IRA-900) in DMF to react the terminal oxazolinium groups with hydroxide ion and to remove tetrafluoroborate ion. After filtration, the product was recovered from the solution and purified by repeated reprecipitations from CH_3CN (solvent) to Et_2O (precipitant). After drying in vacuo, brown solid products were obtained in a yield of 0.289 g (68 %): ^1H NMR δ 0.8-1.2 ($C-CH_3$), 1.3-2.5 ($C-CH_2$ and $C(O)-CH_3$), 2.8-3.1 ($N-CH_3$), 3.1-3.8 ($N-CH_2$ and $O-CH_3$. IR (KBr) 2980, 2950, 1728 ($\nu_{c=o}$, amide), 1630 ($\nu_{c=o}$, ester), 1438, 1240, 1147, 1058, 733 cm^{-1}.

In a similar procedure of 2b with the oxazolines a gelled product was sometimes formed. It was separated and washed with CH_3CN in a Soxhlet's extractor, and dried. Then, a brown resinous solid (insoluble in CH_3CN) was isolated. The extract, combined with the solution part of the reaction mixture, was concentrated and submitted to the above reprecipitation followed by purification. After drying, a brown solid product was isolated which was soluble in CH_3CN and DMF.

Table 1. Preparations of the copolymers 2[a] and the reaction with amine[b]

	Reaction Conditions				Product 2				Amine treated product			
Run No	Comonomer	Feed ratio 1/ester	Temp. (°C)	Time (hr)	Structure	Yield (wt %)	Unit ratio onium/ester	$\eta_{sp/C}$[c] (dL/g)	Structure	$\eta_{sp/C}$[c] (dL/g)	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
1	MMA	0.18	80	15	2a-1	48	0.21	0.18	3a-1	0.19	10,600	1.90
2	MMA	0.50	80	15	2a-2	41	0.41	0.096	3a-2[e]	0.11	5,110	1.88
3	MA	0.10	85	5	2b-1	52	0.085	0.26	3b-1	0.30	> 20,000[f]	---
4	MA	0.18	60	10	2b-2	46	0.17	0.15	3b-2[g]	0.17	8,920	2.35

[a] AIBN 2 mol %, in DMF. [b] 2 was reacted with a five fold molar amount of t-butylamine in CH_3CN.
[c] [C]= 0.12 g/dL, in 2% NaI- CH_3CN sol. at 30 °C. [d] Estimated by GPC analysis from polystyrene standards.
[e] ^1H NMR (CD_3CN) δ 0.7-1.4 ($C-CH_3$), 1.6-2.3 ($C-CH_2-C$, and NH), 2.4-2.7 ($NH-\underline{CH_2}$), 2.8-3.0 ($N-CH_3$), 3.1-3.3 ($N(CO)-CH_2$), 3.3-3.6 (O-Me); IR (KBr) 3420, 2995, 2950, 1725, 1615, 1440, 1240, 1146, 750 cm^{-1}. [f] The molecular weight partly distributed over the exclusion limit of the column. [g] ^1H NMR ($CDCl_3$) δ 0.8-1.4 ($C-CH_3$), 1.5-2.5 ($C-CH_2-C$, CO-CH, and NH), 2.5-2.7 ($NH-\underline{CH_2}$), 2.9-3.3 ($N-CH_3$ and $N(CO)-CH_2$), 3.4-3.7 (O-Me).

5b-2: ^{1}H NMR (CD_3CN) 0.7-1.3 ($C-CH_3$), 1.3-2.6 ($C-CH_2$, $CO-CH_3$, and CO-CH), 2.9-3.2 ($N-CH_3$), 3.3-4.0 ($N-CH_2$ and $O-CH_3$); IR (KBr) 2950, 1740 ($\nu_{c=o}$, amide), 1630 ($\nu_{c=o}$, ester), 1419, 1234, 1052, 748, 598 cm^{-1}.
5c: ^{1}H NMR (CD_3CN) δ 0.7-1.4 ($C-CH_3$), 1.3-2.6 ($C-CH_2$ and CO-CH), 3.0-4.0 ($N-CH_3$, $N-CH_2$, and $O-CH_3$); IR (KBr) 2950, 1725 ($\nu_{c=o}$, ester), 1620 ($\nu_{c=o}$, amide), 1440, 915, 828, 732 cm^{-1}.

Results and Discussion

Graft copolymerization of **4a** onto **2a**. The two samples of **2a** were employed to initiate the polymerization of **4a** in CH_3CN at 80 °C, with the feed ratio of the monomer to the total amount of oxazolinium groups of **2a** being 5 to 10. After 10 hr, the product was isolated. Some results are shown in Table 2.

Table 2
Graft copolymerization of **4a** onto **2a** copolymers

Run No	Feed				Product					
	2	(g)	**4a** (g)	**4a**/onium ion[a]	**5**	Yield (g)	Unit ratio[b]	$\eta_{sp/C}$[c]	$\bar{M}_n$[d]	average graft length[e]
1	**2a-1**	0.39	0.48	10	**5a-1**	0.78	1.6	0.32	14,300	8.8
2	**2a-2**	0.43	0.38	5	**5a-2**	0.68	0.41	0.12	7,050	4.3
3	**2a-2**	0.45	0.83	10	**5a-3**	1.12	0.88	0.21	8,400	9.2

[a] Molar ratio of **4a** to oxazolinium unit in **2a**.
[b] The unit ratio of (N-acetyl)iminoethylene to ester, determined from ^{1}H NMR and elemental analysis of nitrogen.
[c] [C]=0.12 g/dL, in CH_3CN at 30 °C.
[d] Determined from GPC by using polystyrene standards.
[e] Calculated from the monomer feed and the composition of **5a**.

The yield of the product in every run was over 84% after the repeated reprecipitations. By the ^{1}H NMR and IR spectroscopies (Experimental), these products were found to consist of both methacrylate and (N-acetyl)-iminoethylene chains. Thus, the structure **5a** was supported. The graft structure was qualitatively confirmed by the solubility characteristics and the GPC analysis. In Table 3 the solubility of **5a** was compared with that of the parent copolymer **2a** and other related homopolymers, i.e., poly[(N-acetyl)iminoethylene] (**6a**) and poly(MMA).

In Figure 1 the GPC curve of the product was compared with that of **3a**. The GPC curve of the graft copolymer **5a-1** (curve b) appeared at a higher molecular weight position in comparison with that of **3a-1** (curve a). The two curves are of a similar unimodal. Since the molecular weight and molecular weight distribution of **3a** are resomably assumed to be similar to these of **2a**, the shift of GPC curve is taken to support the formation of graft copolymer.

Table 3
Solubility Characteristics of the copolymers 2a, 5a, and the related homopolymers

Solvent	2a	5a	6a	poly(MMA)
Water	-	±	++	-
MeOH	+	+	++	-
MeCN	+	++	++	+
$CHCl_3$	-	+	+	+
C_6H_6	-	-	±	+

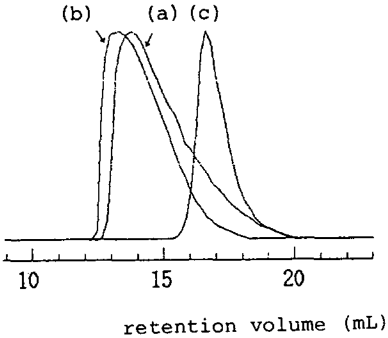


Figure 1. Gel permeation Chromatograms of 2a-1 (a), 5a-1 (b), and 6a (c) (Shodex GPC-A803 column, $CHCl_3$; 1.0 mL/min).

The average length of poly[(N-acyl)iminoethylene] branch was estimated on the assumption that all of the pendant oxazolinium functionalities participated in the initiation of the graft polymerization of 4a. In 5a the unit ratio of (N-acylimino)ethylene to MMA was determined by the ^{1}H NMR spectrum and elemental analysis. This ratio was multiplied by the unit ratios of MMA to the oxazolinium ring of the parent copolymers 2a. The product value represents the average degree of polymerization of (N-acyl)iminoethylene chains which was introduced per one oxazolinium ring of 2a. The values of the average graft length thus obtained for 5a were 8.8 (5a-1), 4.3 (5a-2), and 9.2 (5a-3), respectively, which was a little lower than the calculated value based on the monomer feed ratio.

The average length of branches was determined after the branches were detached from the main chain by alkaline hydrolysis. After alkaline hydrolysis of the graft copolymer 5a-1 with aq. NaOH, the poly(iminoethylene) produced was re-acetylated thoroughly with an excess amount of acetic anhydride to improve its solubility. The resulting poly[(N-acetyl)iminoethylene] (6a') was isolated by the reprecipitation from the reaction mixture to an 1:1 (vol) mixture of diethyl ether and petr. ether. The yield was 60% yield based on (N-acetylimino)ethylene unit of 5a-1. The molecular weight of 6a', which was determined from VPO, was 650. The degree of the polymerization of 6a' was calculated at 7.7 which is in good agreement with the value calculated from the average graft length of 5a-1.

The GPC curve of 6a' is also shown in Figure 1. Narrow molecular weight distribution of 6a' means the rapid initiation of grafting. Considering the average length of graft branches is high enough, every oxazolinium in the pendant group of the parent copolymer has been involved in the initiation. In addition, no homopolymer of 4a was formed, i.e., no soluble polymeric substance was found in a precipitant mixture of CH_2Cl_2/Et_2O.

The average molecular weight of 5a measured by GPC were lower than that predicted from the graft lengths and the molecular weight of the parent copolymers 2. This may be due to the shrank conformation of the polymer chain in solution as has usually been observed with many graft copolymers (4).

Graft copolymerization of oxazolines onto 2b.

The graft copolymerization onto 2b was also examined with three oxazoline monomers. The results are shown in Table 4. When 4a was polymerized, an insoluble yellow gel was sometimes formed (Runs No 2 and 3). In Run No 1 with a lower feed ratio and in Run No 4 at a lower reaction temperature, soluble polymer was the main product. These soluble products were shown to have a graft structure of 5b. They showed a relatively large viscosity in comparison wigh those of the parent copolymer 2b, which is taken to be indicative of a small extent of crosslinking. The insoluble gel was considered to consist of the same constituents from IR measurements. Their insolubility is therefore due to crosslinking.

Table 4

Graft copolymerization[a] of 4 onto 2b

No	Copolymer 2	Feed (g)	Oxazoline 4	Feed (g)	$[M]/[I]$	Temp. (°C)	Time (hr)	Total Yield (g)	Graft copolymer 5	Yield (g)	Unit ratio	$\eta_{sp/C}$	Gel Yield (g)
1	2b-1	0.40	4a	0.14	5	80	10	0.35	5b-1	0.28	0.73	0.47	0.07
2	2b-1	0.40	4a	0.28	10	80	10	0.68	--	0	---	----	0.65
3	2b-2	0.33	4a	0.39	10	60	12	0.57	5b-2	0.35	0.72	2.58	0.18
4	2b-2	0.38	4a	0.44	10	80	10	0.80	--	0	---	----	0.78
5	2b-2	0.37	4b	0.54	10	70	40	0.49	5c	0.26	0.66	0.25	0

[a] In CH_3CN, at 80°C, 10 hr.

In the polymerization of 4b by 2b, only soluble graft copolymer (5c) was obtained, although the yield was much low even after a longer reaction time. The rate of propagation was so low that the graft length was only about 4.8.

The gel formation in the polymerization of 4a by 2b may be ascribed to the reaction of 4a with MA unit in the parent copolymer. The proton of the methyne adjacent to the carbonyl group can be abstracted by a nucleophile of 4a. The carbanion thus produced in the main chain may cause crosslinking by its reaction either with oxazolinium propagating end or with ester group. This type of crosslinking does not occur in the reaction of 2a, which has not hydrogen atom to be abstracted.

References

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