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Cationic Graft Polymerization of 2-Oxazolines on Cellulose Derivatives

Isao IKEDA, Yoshiaki KURUSHIMA,* Hisataka TAKASHIMA,** and Kimihiro SUZUKI

Department of Applied Chemistry, Fukui University, Bunkyo, Fukui 910, Japan

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ABSTRACT: Cationic graft polymerization of 2-oxazolines on cellulose derivatives such as chlorinated cellulose (Cell-Cl), cellulose acetate halogenacetate (AcCell-AcX), and cellulose tosylate (Cell-OTs) was investigated. With Cell-Cl the successful graft polymerization of 2-methyl-2-oxazoline (MeOXZ) required the presence of potassium salt but with AcCell-AcX and Cell-OTs it proceeded without the salt. The reactivity of halogens in graft polymerization of MeOXZ on halogenated cellulose derivatives increased in the order of $I^- > Br^- > Cl^-$. This is explained by the nucleophilicity of halogen ions compared with that of MeOXZ. Graft copolymers prepared with AcCell-AcX were hydrolyzed by 0.5 *N* NaOH solution to isolate the branched poly(MeOXZ). The molecular weight of the branched poly(MeOXZ) measured by GPC was in the range of 380 to 3510 depending on the reaction conditions. 2-Oxazoline (OXZ) did not graft-polymerize with halogenated cellulose derivatives, but graft-polymerized with Cell-OTs.

KEY WORDS Cationic Graft Polymerization / 2-Oxazolines / Cellulose Derivative / Graft Copolymer / Poly(*N*-acylethyleneimine) / Halogen Exchange / Linear Poly(ethyleneimine) /

Ring-opening polymerization of 2-oxazolines has been widely investigated by Saegusa and co-workers. As initiators they used low molecular compounds such as methyl tosylate and methyl iodide to elucidate the mechanism of the polymerization[1] and several polymeric derivatives to synthesize the block and graft copolymers. The polymeric derivatives used were tosyl or mesyl derivatives of poly(ethylene oxide),[2] α, ω-polybutadiene glycol,[3] cellulose,[4] cellulose acetate,[4] and ethylene–vinylacetate copolymer,[5] 1-chlorobutadiene–butadiene copolymer,[6] chloromethylated polystyrene,[7] bromoacetylated hydroxyethyl cellulose[8], etc. Furthermore, the product copolymers were hydrolyzed with concentrated sodium hydroxide solution to convert the poly(*N*-acylethyleneimine) component into poly(ethyleneimine) (PEI). The converted copolymers were used as an adsorbent of heavy metal ions.[7]

As previously reported,[9,10] we demonstrated that graft and/or cross-linked copolymers were prepared by the reaction of commercial PEI with cellulose derivatives such as Cell-Cl, AcCell-AcX, and Cell-OTs or bromoacetalized poly(vinyl alcohol). The product copolymers were used as adsorbents of heavy metal ions and supporting materials of enzymes. Apparently, these three cellulose derivatives are also the initiators of 2-oxazoline polymerizations. In the graft polymerization of 2-oxazolines the prepared copolymers can have the well-defined structure by the conversion of

* Present address: *Research and Development Center of Unichika Ltd., Kozakura, Uji, Kyoto 611, Japan.*
** Present address: *Urase Goudou Senkou Ltd., Kaminaka-cho, Sabae, Fukui 910, Japan.*

poly(*N*-acylethyleneimine) to linear PEI but it is difficult to control the molecular weights of branched polymers contrary to the reaction of commercial PEI. Thus there have not been studies concerning the structures of graft copolymers such as the length of branched polymer and the degree of branching. On the basis of these points, we also investigated the polymerization of 2-oxazolines by these cellulose derivatives. The graft polymerization of 2-oxazolines was performed homogeneously in DMF, nitrobenzene and benzonitrile. The present article describes (1) the differences of the reactivities of 2-oxazolines on the three cellulose derivatives and (2) the determination of molecular weight of branched poly (*N*-acetylethyleneimine) (poly(MeOXZ) separated from the copolymers prepared with AcCell-AcX and apparent initiator efficiency of AcX groups.

EXPERIMENTAL

Materials

MeOXZ was purchased from Aldrich Chem. Co. and purified by distillation. OXZ was synthesized according to the method of Wenker,[11] Franco,[12] and Saegusa[13] and purified by distillation. Cell-Cl, AcCell-AcX, and Cell-OTs were synthesized by the following methods. Cell-Cl[14]: regenerated cellulose (3 g) prepared by the saponification of cellulose acetate ($\overline{DP}=169$) was dissolved in a mixture of chloral (10 ml) and DMF (100 ml). Then methanesulfonyl chloride (11.6 ml) was added to the solution and reacted for 4 hours at 75°C under a nitrogen atmosphere. The products were precipitated in water, neutralized with 10% sodium carbonate, filtered off, washed with water and dried in the vaccum oven. $\overline{DP}$ of Cell-Cl (Cl% = 26.1) was 48. AcCell-AcX[15]: cellulose acetate (5 g) was dissolved in halogenated acetic acid at 60—85°C. Then sodium acetate (2.5 g) and acetic anhydride (11.2 g) were slowly added to the solution and the reaction mixture was maintained at 80°C for 5 hours. The products were precipitated in water, washed with water until the free acid was not detected and purified by reprecipitation (methylene chloride/methanol). $\overline{DP}$ of AcCell-AcCl (DS of AcCl = 0.27), AcCell-AcBr (DS of AcBr = 0.22), and AcCell-AcI (DS of AcI = 0.19) were 56, 33, and 48, respectively. Cell-OTs[16]: regenerated cellulose (2 g) was immersed in the mixture of pyridine (30 ml) and water (10 ml) in order to activate itself. Then the activated cellulose was immersed in pyridine for 2 hours to remove the remained water. After this operation was repeated four times, tosyl chloride (14 g) was added to the activated cellulose and the reaction was continued for seven days at room temperature. The products were precipitated in ethanol and washed with ethanol using Soxhlet extraction for 24 hours. $\overline{DP}$ of Cell-OTs (DS of OTs = 2.8) was 21. Solvents such as DMF, nitrobenzene and benzonitrile were purified by conventional methods. Commercial potassium iodide and potassium bromide were used without further purification.

Graft Polymerization of 2-Oxazolines on Cellulose Derivatives

Graft polymerization was carried out in a pear-shaped flask equipped with a three-way cock under a dry nitrogen atmosphere. Cellulose derivative (0.4 g) was dissolved in a polar solvent (8—20 ml) and then a monomer (2—4 ml) and internal standard regent of gas chromatography (2 ml) were added to the solution. The solution was heated at 100°C (with MeOXZ) or 90°C (with OXZ) for 24 hours with stirring. After the reaction, the products were precipitated in ether, filtered off and washed with water to remove the homopolymer of 2-oxazolines using Soxhlet extraction above 24 hours. Conversion of 2-oxazolines was determined from the residual monomer concentration by gas chromatography using bromobenzene or tetraline as internal standard. The composition of copolymers (represented by the molar ratio of monomer unit to

cellulose derivative unit, [monomer]/[cellulose derivative]) was assayed by nitrogen analysis, the Kjeldahl's method being used and calculated from eq 1.

$$\text{[monomer]/[cellulose derivative] in copolymer} = \frac{N \times \text{unit molecular weight of cellulose derivative}}{1400 - N \times \text{molecular weight of monomer}} \quad (1)$$

(N: N% of copolymer)

Isolation of Branched Poly(MeOXZ) from Copolymers

Isolation of branched poly(MeOXZ) from copolymers (0.3 g) synthesized by the graft polymerization of MeOXZ on AcCell-AcX were carried out in the following manner: (1) swelling in 75% aqueous ethanol (10 ml) at 50—60°C for 30 minutes, (2) addition of 0.5 N NaOH (16 ml) and (3) heating on the steam bath for 10 minutes and standing at room temperature for 24 hours. Acetyl groups of AcCell-AcX will be hydrolyzed by this reaction, resulting in the separation of branched poly(MeOXZ). After the reaction, the solution was neutralized with 1 N HCl, concentrated, exchanged water with methanol and poured into chloroform. Salts formed were filtered off and the filtrate was concentrated. Branched poly(MeOXZ) precipitated by addition of the concentrated filtrate into ether.

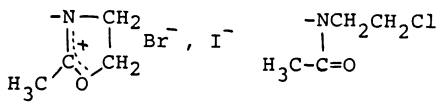
Determination of Molecular Weight

Number-average molecular weights ($\bar{M}_n$) of cellulose derivatives and branched poly (MeOXZ) were measured by gel permeation chromatography (GPC; Toyo Soda Model HLC-803D, GMHXL polystyrene gel columns, DMF solution). Mn was calculated from GPC curves on the basis of a polyethyleneoxide calibration.

RESULTS AND DISCUSSION

Graft Polymerization of MeOXZ on Cell-Cl

Effect of KI Addition on Graft Polymerization. In the ring-opening polymerization of MeOXZ, it has been shown that the polymerization initiated by iodide or bromide compounds such as methyl iodide and benzyl bromide proceeds *via* ionic propagating species **1** but that initiated by chlorine compounds proceeds *via* covalent species **2** due to the nucleophilicity of halogen anion.[17] Accordingly, the rate of polymerization of the former is larger than that of the latter. With chlorine compounds, however, it is possible to enlarge the rate of polymerization of MeOXZ by the addition of salts such as potassium iodide due to the anion-exchange reaction.



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Then, the graft polymerization of MeOXZ on Cell-Cl was carried out in the presence of potassium iodide. Figure 1 shows that the graft polymerization hardly occurred in the absence

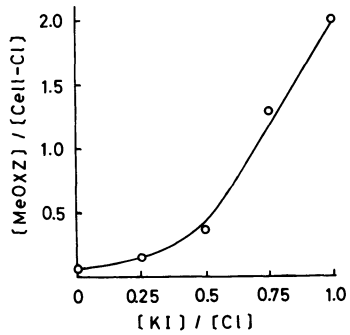

Figure 1. Acceleration of graft polymerization of MeOXZ on Cell-Cl by addition of KI: [Cell-Cl(Cl% = 16.6)], 0.10 mol l^{-1}; [MeOXZ], 1 mol l^{-1}; DMF, 20 ml; temp, 100°C; time, 24 h.

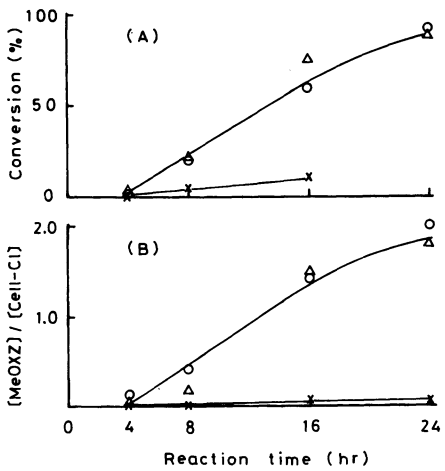

Figure 2. Effect of reaction temperature on the rates of polymerization (A) and graft polymerization (B) of MeOXZ: [Cell-Cl(Cl% = 26.1)], 0.09 mol l^{-1}; [MeOXZ], 1 mol l^{-1}; [KI]/[Cl] = 1.0; DMF, 20 ml. Temperature: (○) 100°C; (△) 80°C; (×) 60°C.

of potassium iodide and that the molar ratio of [MeOXZ]/[Cell-Cl]increased with an increase in the amount of potassium iodide. This shows that the halogen-exchange reaction of Cl to I is necessary to initiate this graft polymerization.

Effect of Reaction Temperature on the Rate of Graft Polymerization. The graft polymerization of MeOXZ on Cell-Cl was carried out at 60, 80, and 100°C in the presence of potassium iodide of equimolar amounts with Cl. The curves of the rate of polymerization and the rate of graft polymerization were shown in Figure 2. MeOXZ hardly polymerized at 60°C, but easily polymerized at 80°C and 100°C. The rates of polymerization over 80°C were not affected by the temperature. The grafting efficiency of MeOXZ, defined by eq 2, was about 20% at each reaction time.

$$\text{grafting efficiency (\%)} = \frac{\text{the amount of grafted MeOXZ}}{\text{the amount of polymerized MeOXZ}} \times 100 \quad (2)$$

Effect of Monomer Concentration on Graft Polymerization. The graft polymerization of MeOXZ on Cell-Cl was carried out in the presence of potassium iodide of equimolar amounts with Cl at various MeOXZ concentrations in DMF. As shown in Figure 3, [MeOXZ]/[Cell-Cl] increased proportionally with an increase in MeOXZ concentration.

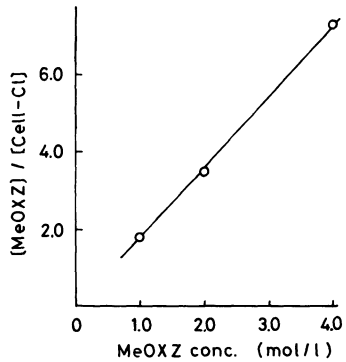

Figure 3. Effect of MeOXZ concentration on graft polymerization of MeOXZ on Cell-Cl: [Cell-Cl(Cl% = 26.1)], 0.18 mol l^{-1}; [KI]/[Cl] = 1.0; solvent; DMF; temp, 100°C; time, 24 h.

Table I. Graft polymerization of MeOXZ on Cell-Cl in various solvents[a]

Solvent	Copolymer composition	
	N/%	[MeOXZ]/[Cell-Cl]
DMF	12.6	7.3
Nitrobenzene	11.1	4.7
Benzonitrile	11.9	5.8

[a] [Cell-Cl(Cl% = 26.1)], 0.18 mol l^{-1}; [MeOXZ], 3.9 mol l^{-1}; solvent, 8 ml; [KI]/[Cl] = 1.0; temp, 100°C; time, 24 h.

Effect of Solvent on Graft Polymerization. The graft polymerization of MeOXZ on Cell-Cl was carried out in nitrobenzene and benzonitrile, as well as DMF. As shown in Table I, [MeOXZ]/[Cell-Cl] revealed the maximum value in DMF. This is probably due to the difference of solubility of Cell-Cl and copolymer in the three solvents. It is to be noted that the graft polymerization did not occur in the absence of potassium iodide in any solvent.

Table II. Graft polymerization of MeOXZ on AcCell-AcX in the presence or absence of potassium salts in DMF[a]

AcX	Salt	Conversion of MeOXZ	[MeOXZ]/[AcCell-AcX] in copolymer	Grafting efficiency	$\bar{M}_n$ of branched poly(MeOXZ)	Apparent initiator efficiency
		%		%		%
AcCl	—	29	1.0	22	570	55
	KBr	64	2.3	23	1110	65
	KI	94	3.9	26	1430	86
AcBr	—	78	2.2	16	1070	43
	KI	99	3.3	19	1350	51
AcI	—	—	3.7	—	1580	54

[a] [AcCell-AcX], 0.06 mol l^{-1}; DS of AcX, AcCl: 0.27, AcBr: 0.41, AcI: 0.37; [MeOXZ], 1 mol l^{-1}; DMF, 20 ml; temp, 100°C; time, 24 h.

Graft Polymerization of 2-Oxazolines on AcCell-AcX

Effect of the Kind of AcX and the Addition of Salts on Graft Polymerization. The graft polymerization of MeOXZ and OXZ on AcCell-AcX, where X is composed of Cl, Br or I was carried out in the presence or absence of potassium salts. Though MeOXZ cannot graft-polymerize on Cell-Cl in the absence of potassium iodide as mentioned in previous section, it can graft-polymerize on AcCell-AcCl under the same conditions as shown in Table II. This is presumably due to the large reactivity of α-chloroesters of AcCell-AcCl in the nucleophile reaction of MeOXZ.

MeOXZ polymerized more easily in the presence of KBr or KI resulting in the higher MeOXZ conversion and [MeOXZ]/[AcCell-AcCl]. These values were in the order of non-salt < KBr < KI, namely $Cl^- < Br^- < I^-$ as a counter anion of propagating species. Though the polymerization of MeOXZ was easily initiated by AcCell-AcCl, it is considered that it was also easily terminated because of the large nucleophilicity of Cl^- ion. As a result, this graft polymerization is considered to be affected by the nucleophilicity of halogen ions compared with that of MeOXZ, $Cl^- >$ MeOXZ $> Br^- > I^-$.[1] Accordingly with AcCell-AcBr MeOXZ polymerized sufficiently without the addition of KI but [MeOXZ]/[AcCell-AcBr] enlarged further in the presence of KI.

Table III. Graft polymerization of OXZ on AcCell-AcX in DMF[a]

AcX	Conversion of OXZ	[OXZ]/[AcCell-AcX] in copolymer	Grafting efficiency
	%		%
AcCl	2.5	0.04	8
AcBr	2.7	0.06	11
AcI	—	0.09	—

[a] Polymerization conditions are the same as in Table II except that the reaction temperature is 90°C.

Thus the graft polymerization of MeOXZ on AcCell-AcX proceeded easily in the order of $Cl^- < Br^- < I^-$ counter anion, that is in the reverse order of nucleophilicity of anions.

On the other hand, the polymerization of OXZ hardly occurred with any AcCell-AcX as shown in Table III. This is probably due to smaller nucleophilicity of OXZ compared with that of the three halogen anions.[1]

Then the graft copolymers were hydrolyzed according to the method mentioned in the experimental section in order to isolate the branched polymer. No nitrogen was detected from the remaining polymer by elemental analysis and the polymer recovered from solution

was well confirmed to be poly(MeOXZ) by IR and ^{1}H NMR spectra. As shown in Table II, the molecular weight ($\bar{M}_n$) of branched poly(MeOXZ) determined by GPC was less than 1580 (DP, 18.6) and was in the order of $Cl^- < Br^- < I^-$. The order of apparent initiator efficiency of halogen acetyl group calculated from equation (3) was also consistent with this order.

$$\text{apparent initiator efficiency (\%)} = \frac{[\text{MeOXZ}]/[\text{AcCell-AcX}] \text{ in copolymer} \times 8500}{\text{degree of substitution (DS) of AcX} \times \bar{M}_n \text{ of branched poly(MeOXZ)}} \quad (3)$$

From these results, it is apparent that the ease of graft polymerization of MeOXZ on AcCell-AcX increases with decreasing nucleophilicity of halogen ions.

Effect of the DS of AcX. The graft polymerization of MeOXZ was carried out with AcCell-AcX having different DS of AcX. Table IV shows that the conversion of MeOXZ and [MeOXZ]/[AcCell-AcX] increased with an increase in the DS of AcX, that is, the initiator concentration. $\bar{M}_n$ of branched poly(MeOXZ), however, decreased with increasing in the DS of AcX resulting in an increase in the apparent initiator efficiency. This means that the graft copolymers have shorter and numerous branched poly(MeOXZ) chains on increasing the DS of AcX.

Effect of MeOXZ Concentration. The graft polymerization of MeOXZ on AcCell-AcBr was carried out at various MeOXZ concentrations. As shown in Table V, [MeOXZ]/[AcCell-AcBr] and $\bar{M}_n$ of branched poly(MeOXZ) increased with increasing MeOXZ concentration, but the apparent initiator efficiency of AcBr was almost constant. This means that the graft copolymers have longer branched chains with increasing MeOXZ concentration resulting in an increase in

Table IV. Graft polymerization of MeOXZ on AcCell-AcX having various DS of AcX in DMF[a]

AcX	DS of AcX	Conversion of MeOXZ	[MeOXZ]/[AcCell-AcX] in copolymer	Grafting efficiency	$\bar{M}_n$ of branched poly(MeOXZ)	Apparent initiator efficiency
		%		%		%
AcBr	0.22	27	0.8	18	1130	26
	0.41	78	2.2	16	1070	43
	0.62	65	4.2	34	800	71
AcI	0.19	92	2.9	19	3510	37
	0.37	—	3.7	—	1580	54

[a] [AcCell-AcX], 0.05—0.06 mol l^{-1}; [MeOXZ], 1 mol l^{-1}; DMF, 20 ml; temp, 100°C; time, 24 h.

Table V. Graft polymerization of MeOXZ on AcCell-AcBr at various MeOXZ concentrations in DMF[a]

MeOXZ conc.	Conversion of MeOXZ	[MeOXZ]/[AcCell-AcBr] in copolymer	Grafting efficiency	$\bar{M}_n$ of branched poly(MeOXZ)	Apparent efficiency
mol l^{-1}	%		%		%
0.25	61	1.7	58	380	60
0.5	61	2.3	40	550	58
1.0	65	4.2	34	800	71

[a] [AcCell-AcBr (DS of AcBr = 0.62)], 0.05 mol l^{-1}; DMF, 20 ml; temp, 100°C; time, 24 h.

Table VI. Graft polymerization of 2-oxazolines on Cell-OTs in various solvents[a]

Monomer	Solvent	Conversion of monomer	[Monomer]/[Cell-OTs] in copolymer	Grafting efficiency
		%		%
MeOXZ	DMF	32	2.9	28
	Nitrobenzene	53	5.0	27
	Benzonitrile	94	6.1	18
OXZ	DMF	2	0.7	84
	Nitrobenzene	12	1.2	24
	Benzonitrile	6	1.3	57

[a] [Cell-OTs (DS of OTs = 2.8)], 0.03 mol l^{-1}; [monomer], 1 mol l^{-1}; solvent, 20 ml; temp, 100°C (MeOXZ) or 90°C (OXZ); time, 24 h.

[MeOXZ]/[AcCell-AcBr].

Graft Polymerization of 2-Oxazolines on Cell-OTs

The graft polymerization of MeOXZ and OXZ on Cell-OTs was carried out in DMF, nitrobenzene and benzonitrile. Both monomers graft-polymerized on Cell-OTs in these three solvents and the molar ratio of [monomer]/[Cell-OTs] was greater with MeOXZ than with OXZ as shown in Table VI. OXZ did not graft-polymerize on AcCell-AcX as shown in Table III, but graft-polymerized on Cell-OTs.

On the graft polymerization of MeOXZ on Cell-OTs having various DS of OTs groups in benzonitrile, [MeOXZ]/[Cell-OTs] was almost constant in the range of DS 1.7 to 2.8. This is probably due to the sufficient concentration range for this initiator to reach maximum [MeOXZ]/[Cell-OTs]. Figure 4 shows ^{1}H NMR spectra of the copolymer and Cell-OTs. The spectrum of the copolymer revealed a characteristic peak of acetyl group in poly(MeOXZ) at about 2.0 ppm.

Then the copolymer was hydrolyzed in *ca.* 8% sodium hydroxide solution at 100°C for 48 hours to convert the grafted poly(MeOXZ) to PEI according to the Saegusa's method.[7] The copolymer composed of 87 mol% poly(MeOXZ) was acertained to contain 85 mol% PEI after hydrolysis from the elemental analysis. Futher, the ^{1}H-NMR spectrum of the copolymer revealed a new peak of the methylene group in PEI at about 2.8 ppm instead of the dissapearance of acetyl peak in poly(MeOXZ).[18]

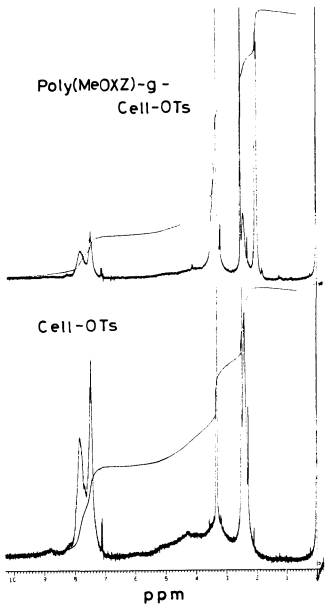

Figure 4. ^{1}H NMR spectra of Cell-OTs and poly(MeOXZ)-*g*-Cell-OTs in DMSO-d_6 (recorded on JEOL-GX 270 spectrometer).

From these results, it is apparent that the graft copolymers composed of linear PEI as branched polymer could be synthesized by this method. These graft copolymers have well-

defined structures different from the copolymers synthesized by the reaction of Cell-OTs with commercial PEI constituted of branched structure.[9]

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