

Synthesis of Poly[ethylene-co-(vinyl acetate)-g-(2-alkyl-2-oxazoline)]s

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ABSTRACT: For preparation of a graft copolymer having a polyethylene main chain and poly(*N*-acylethylenimine) graft chain, poly[ethylene-co-(vinylacetate)-g-(2-alkyl-2-oxazoline)]s (**4**) were prepared. First, poly[ethylene-co-(vinyl acetate)] (**1**) was saponified to give polymer (**2**) having a hydroxy group. Secondly, **2** was tosylated or bromoacetylated giving rise to polymer (**3a**) or (**3b**). Then, polymer **3** was employed to initiate the cationic ring-opening polymerization of 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline to produce a graft copolymer which was isolated by reprecipitation. During the graft copolymerization, a homopolymer of 2-oxazoline was produced probably due to chain-transfer, the highest graft-efficiency being 50%.

KEY WORDS Poly(2-oxazoline) Graft Copolymer / Poly[ethyl-co-vinyl acetate)] / Vinyl Alcohol Unit / Tosylation / Bromoacetylation /

Polymerization chemistry of 2-oxazolines and other cyclic imino ether monomers has greatly developed for these two decades. The cationic ring-opening polymerization of 2-alkyl-2-oxazolines produces poly(*N*-acylethylenimine)s and their hydrolysis gives linear polyethylenimine.¹ Through our recent studies on the polymerization of 2-oxazolines² we observed the following characteristic features; i) polymerization can be initiated by alkyl sulfonates or alkyl halides, ii) propagation is of a highly living nature, and iii) the product poly(*N*-acylethylenimine) is hydrophilic or lipophilic depending upon the nature of the acyl group. Based on these characteristics, various block and graft copolymers of 2-oxazolines have been prepared.^{1,2} Several papers have reported graft copolymers from 2-oxazolines: poly[styrene-g-(2-methyl-2-oxazoline)],^{3,4} poly[butadiene-g-(2-methyl-2-oxa-

zoline)],⁵ poly[(vinyl chloride)-g-(2-methyl-2-oxazoline)]⁶ poly[(2-phenyl-2-oxazoline)-g-(ethylene oxide)],⁷ and cellulose diacetate-g-poly(2-alkyl-2-oxazolines),⁸ and poly[methyl methacrylate-g-(2-oxazoline)]s.⁹ We also prepared graft copolymers having poly(2-oxazoline) segments both in the main and graft chains, which show good surfactant nature reflected by a surface tension (γ) value.¹⁰ The present paper describes the synthesis of graft copolymers having poly[ethylene-co-(vinylacetate)] [poly(E-co-VAc)] main chain and poly(2-alkyl-2-oxazoline) (polyROZO) graft chain, which is an extension study of the synthesis of graft copolymers from 2-oxazolines.^{3-5,7-10} The main purpose of this study is to modify the surface nature of polyethylene by introducing the graft chain of poly(*N*-acylethylenimine).

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EXPERIMENTAL

Materials

MeOZO (Aldrich Co.) and EtOZO (supplied by Dow Chem. Co., Midland) were dried on molecular sieves and distilled under nitrogen. Commercial bromoacetyl chloride and all solvents were purified by distillation under nitrogen after drying. *p*-Toluenesulfonyl chloride (TsCl) was used as received.

Copolymers, poly(E-*co*-VAc) **1** ($M_n = 15,600$) and saponified polymer **2-5**, were supplied by Japan Synthetic Chem. Co. (Ibaragi, Osaka). *Anal.* for **1**: C, 69.30%; H, 10.31%. This result leads to the composition E/VAc = 71.7/28.3. *Anal.* for **2-5**: C, 63.23%; H, 10.59%, leading to the composition E/VA/VAc = 38.0/61.0/0.4. ^1H NMR spectrum of **1** in C_6D_6 showed acetyl signals at δ 1.80 ppm due to E/VAc dyad and at δ 1.88 ppm due to VAc/VAc dyad,¹¹ and the ratio was 71.4/28.6, which is very close to that obtained by elemental analysis.

Saponification of Copolymer 1

A typical run of the saponification of **1** to sample code **2-3** was carried out as follows. A mixture of copolymer **1** (44.40 g) in methanol (260 ml) and NaOH (0.34 g) in methanol (30 ml) was refluxed for 50 min with stirring. After the reaction, the mixture formed two layers, a highly viscous polymer layer and a methanol layer. With cooling, the polymer layer became solidified, which was separated by filtration, washed with methanol, water, and again methanol, and dried at 50°C *in vacuo* to give a solid polymer **2-3** (27.74 g). *Anal.* Found: C, 70.95%; H, 11.36%. This result leads to the composition of E/VA/VAc = 71.7/12.7/15.6, and hence, the degree of hydrolysis of acetate group is 44.9%. ^1H NMR spectrum of polymer **2-3** in pyridine showed a peak due to acetyl group at δ 2.03 ppm and a signal due to the methylene protons of the main chain at δ 1.23 ppm. The integral ratio of these two peaks gave the composition, E/VA/VAc = 71.7/13.6/

14.6, this being very close to that obtained by elemental analysis.

Tosylation of Copolymer 2

A typical procedure to prepare a tosylated polymer **3a-2** was as follows. To 120 ml of pyridine containing TsCl (2.13 g) was added polymer **2-3** (8.00 g) under nitrogen at 0–2°C. The mixture was stirred for 25 h, becoming homogeneous after about 8 h. Then, the homogeneous mixture was poured into a large amount of water to give bulk polymeric materials, which were separated, dissolved in CHCl_3 and washed with aqueous NaHCO_3 and with water. The CHCl_3 solution was dried on Na_2SO_4 , filtered, and poured into a large amount of hexane to precipitate polymeric materials, which were reprecipitated again using CHCl_3 as a good solvent and hexane as a non-solvent and dried *in vacuo*, giving rise to a white polymeric bulk **3a-2** (6.42 g). *Anal.* Found: S, 2.96%. This give the copolymer composition, E/tosylated unit/VA/VAc = 71.7/4.2/8.5/15.6, the degree of tosylation being 33.1%. ^1H NMR analysis of **3a-2** in CDCl_3 was made the basis of aromatic protons (4H, δ 7.28–7.89 ppm, A_2B_2 -type quartet) and of methylene protons (δ 1.23 ppm) to reveal the composition, E/tosylated unit/VA/VAc = 71.7/3.8/8.9/15.6, which is close to the above result.

Bromoacetylation of Copolymer 2

Preparation of **3b-2** is given as a typical example. Bromoacetyl chloride (0.91 g) was added to DMA (70 ml) containing polymer **2-2** (3.03 g), and the mixture was stirred at 40°C for 4 h. Then, the reaction mixture was poured into a large amount of water to precipitate a white polymer solid, which was dissolved in CHCl_3 , dried on Na_2SO_4 , and poured into a large amount of hexane to precipitate the polymer again. The resulting polymer was separated, dried *in vacuo*, once again, purified by reprecipitation from CHCl_3 (solvent)/hexane(non-solvent), and dried *in vacuo* to give a white solid polymer **3b-2** (2.95 g). *Anal.*

Found: Br, 8.21%. This value leads to the polymer composition E/bromoacetylated unit/VA/VAc=71.7/4.5/9.1/14.7, the degree of bromoacetylation being 33.1%. ^1H NMR spectrum (CDCl_3) showed doublet-like signals at δ 3.83 and 4.05 ppm due to bromoacetyl protons and a signal at δ 1.22 ppm assigned to methylene protons of the main chain. The integral ratio of these signals revealed the polymer composition E/bromoacetylated unit/VA/VAc=71.5/5.1/8.5/14.7, which is close to the above value.

Graft Copolymerization

Graft copolymerizations using **3a** or **3b** were carried out similarly. The preparation of graft copolymer **4a-10** is given as a typical example. In a glass tube were placed 0.59 g of polymer **3a-3**, 21.6 ml of PhCN, and 1.55 g of EtOZO under nitrogen. The tube was sealed and heated at 100°C for 13 h. After the reaction, the tube was opened and the reaction mixture concentrated *in vacuo* at 40°C to about 5 ml. To this concentrated solution 6 ml of CHCl_3 were added and the resulting solution was poured into a large amount of hexane to precipitate polymeric materials, which were separated by filtration, washed with cyclohexane, and dried *in vacuo* to give a brittle polymer mixture (2.10 g) of graft copolymer and homopolyEtOZO. The mixture was dissolved in 5 ml of THF and poured into an aqueous solution of NaCl to precipitate a white polymer solid, which was separated by filtration, washed with water and dried *in vacuo*. The reprecipitation procedure using THF (solvent) and the aqueous NaCl solution (non-solvent) was repeated once again giving rise to 0.53 g of graft copolymer **4a-10** after drying *in vacuo*. This graft copolymer sample was dissolved in CHCl_3 and reprecipitated by pouring the solution into hexane. The resulted polymer was separated and dried to give 0.42 g of gummy-like materials, which was used for elemental analysis. The drying procedure above was performed at room temperature every time.

The aqueous NaCl layer after the above reprecipitation was concentrated *in vacuo* and polymeric materials were extracted with CHCl_3 from the concentrated residue. The CHCl_3 layer was dried on Na_2SO_4 and CHCl_3 was evaporated *in vacuo* to give 1.45 g of polymeric solids composed mainly of polyEtOZO.

Measurements

^1H NMR spectra were recorded on a Hitachi R-20B NMR spectrometer (60 MHz). IR spectra were taken using a Hitachi EPIG 31 spectrophotometer. Gel permeation chromatography (GPC) analysis was performed using a JASCO TRIROTOR with a RI detector under the following conditions: a column, Shodex A 804; solvent, chloroform, and flow rate, 1 ml min $^{-1}$. The standard sample of molecular weight determination in GPC analysis was polystyrene.

RESULTS AND DISCUSSION

Preparation Procedure of Poly[ethylene-co-(vinyl acetate)-g-(2-alkyl-2-oxazoline)] (**4**)

We first attempted to prepare poly[ethylene-g-(2-alkyl-2-oxazoline)] so as to modify the surface nature of polyethylene by introducing the graft chain of poly(*N*-acylethylenimine). However, poly(*E-co-VAc*) was found a more readily accessible polymer which allows constructing the polyethylene main chain and introducing tosylate or bromoacetate group for the initiation of the 2-oxazoline polymerization. Therefore, the copolymer was used as a starting polymer in this study. The procedure of preparation of poly[ethylene-co-(vinyl acetate)-g-(2-alkyl-2-oxazoline)](poly(*E-co-VAc-g-ROZO*)) (**4**) is outlined in Scheme I.

Saponification of Poly(*E-co-VAc*) (**1**)

Poly(*E-co-VAc*) (**1**) had a composition of unit ratio, E/VAc=71.7/28.3 ($M_n=15,600$ by vapor pressure osmometry). The saponification of **1** was carried out in methanol containing NaOH at refluxing temperature of methanol

Table II. Tosylation of polymer **2** to polymer **3a**

		Tosylation ^a				Product (3a)			
Sample code	Polymer 2		TsCl	Pyridine	[TsCl] ₀	Sample code	Yield	S ^b	Tosylated unit ^c
	g	(VA, unit mol)	g	ml	[VA] ₀				
2-1	4.00	(0.032)	6.76	70	1.10	3a-1	6.58	8.62	17.8
2-3	8.00	(0.026)	2.13	120	0.43	3a-2	6.42	2.96	4.2
2-4	7.00	(0.007)	2.76	112	2.01	3a-3	4.76	1.46	2.1

^a Reaction at 0–2°C for 25 h.^b Obtained by elemental analysis.^c Calculated from S (%) in the product polymer.**Table III.** Bromoacetylation of polymer **2** to polymer **3b**

		Bromoacetylation ^a				Product (3b)			
Sample code	Polymer 2		BAC	DMA	[BAC] ₀	Sample code	Yield	Br ^b	Bromoacetylated unit ^c
	g	(VA, unit mol)	g	ml	[VA] ₀				
2-5	4.42	(0.071)	12.40	100	1.11	3b-1	9.92	42.62	57.3
2-2	3.03	(0.011)	0.91	70	0.53	3b-2	2.95	8.21	4.5
2-4	4.00	(0.004)	1.07	100	1.70	3b-3	3.40	2.29	1.3

^a Reaction at 40°C for 4 h.^b Obtained by elemental analysis.^c Calculated from Br (%) in the product polymer.

chloroform or benzonitrile.

Bromoacetylation of **2** was performed by bromoacetyl chloride (BAC) in *N,N*-dimethylacetamide (DMA) at 40°C for 4 h to produce polymers (**3b**) containing 57.3–1.3 unit molar percents of bromoacetylated groups (Table III). All polymers (**3b**) were also elastic materials soluble in organic solvents such as dichloromethane, chloroform, benzonitrile and DMA.

Grafting of 2-oxazoline onto Polymer **3**

The cationic ring-opening polymerization of EtOZO or MeOZO was induced by the tosylated or bromoacetylated group of polymer **3a** or **3b**. The polymerization proceeded homogeneously in all cases and the monomer

was consumed completely (Tables IV and V).

In the polymerizations, a homopolymer of EtOZO or MeOZO was produced in addition to the graft copolymer, probably due to a chain-transfer reaction. The production of the homopolymer was confirmed by GPC; GPC chart of product polymers (**4a-3** and **4-4**) showed two peaks at 70,000 and at 2,000–6,000 relative to polystyrene standard. The former peak is ascribed to the graft copolymer and the latter peak to homopolymer of EtOZO. However, it was found that the precipitated graft copolymers (**4a** and **4b**) could be separated as follows. Product polymers were soluble in tetrahydrofuran (THF) and the THF solution of the polymers was poured into a large amount of water. Then, the graft

Table IV. Graft copolymerization of 2-alkyl-2-oxazoline (ROZO) onto polymer 3a^a

Initiator polymer (3a)		ROZO ^b		Yield of polymer mixture ^c		Sample code	Isolated yield	Elemental analysis		Grafted ROZO, mol/X, mol		Graft efficiency ^g	Residual OTs, mol ^e /X, mol
Code	g	R	g	[ROZO] ₀	[X in 3a] ₀			N	S	A ^c	B ^f		
Graft copolymerization													
Graft copolymer (4a)													
3a-2	0.60	Et	0.46	8.4	1.00	4a-1	0.37	1.43	0.18	1.07	1.49	12.8	0.06
	0.60	Et	1.07	19.6	1.60	4a-2	0.35	3.13	0.16	2.70	3.01	13.8	0.06
	0.60	Et	1.46	26.6	2.02	4a-3	0.55	4.31	0	4.13	4.52	15.5	0
	0.60	Et	2.20	40.0	2.76	4a-4	0.39	5.09	0.13	5.35	5.79	13.4	0.06
	0.60	Me	0.75	15.9	1.30	4a-5	0.36 ^d	—	—	—	—	—	—
	0.60	Me	1.22	52.0	1.75	4a-6	0.32 ^d	—	—	—	—	—	—
3a-3	0.60	Et	0.43	15.8	0.98	4a-7	0.45	0.66	0.24	1.02	—	6.5	0.16
	0.60	Et	0.65	23.9	1.19	4a-8	0.52	0.90	0.15	1.41	1.17	5.9	0.10
	0.59	Et	0.98	36.6	1.52	4a-9	0.53	1.69	0.20	2.81	2.43	7.7	0.15
	0.59	Et	1.55	57.7	2.10	4a-10	0.53	3.25	0.17	6.19	5.78	10.7	0.14
	0.59	Me	0.60	26.0	1.14	4a-11	0.50	1.90	0.21	3.32	2.91	12.8	0.16
	0.59	Me	0.88	38.5	1.44	4a-12	0.67	2.92	0	5.60	6.65	14.6	0

^a Solvent, C₆H₅CN (22 ml for 0.60 g of polymer 3a); temp, 100°C; time, 13 h.^b Conversion of ROZO was 100% in all runs.^c Combined amounts of graft copolymer and homopolymer of ROZO.^d Almost insoluble in organic solvents after isolation.^e Calculated by N and S (%) in the graft copolymer from elemental analysis.^f Determined by ¹H NMR spectroscopy.^g [Grafted ROZO(A value)]/[charged ROZO] × 100.

Table V. Graft copolymerization of 2-ethyl-2-oxazoline (EtOZO) onto polymer **3b**^a

Graft copolymerization				Graft copolymer (4b)						
Initiator polymer (3b)	EtOZO ^b	Yield of polymer mixture ^c		Sample code	Isolated yield	Elemental analysis		Grafted EtOZO, mol/		Residual Br, mol ^d /X, mol
		[EtOZO] ₀	[X in 3b] ₀			N	Br	A ^d	B ^e	
Code	g	g	g	g	g	%	%	A ^d	B ^e	%
3b-2	0.50	0.62	12.3	1.08	0.66	5.55	1.87	6.15	5.48	50.0
	0.50	1.03	20.5	1.45	0.43	6.41	1.43	7.87	6.77	38.4
	0.40	1.22	30.2	1.59	0.32	6.71	1.25	8.56	7.58	28.3
3b-3	0.60	1.07	61.1	1.62	0.65	2.75	4.36	8.50	7.76	13.9
	0.60	1.62	92.7	2.13	0.62	3.38	0.89	10.70	11.14	11.5

^a Solvent, C₆H₅CN (22 ml for 0.60 g of polymer **3b**); temp, 100°C; time, 42 h.

^b Conversion of EtOZO was 100% in all runs.

^c Combined amounts of graft copolymer and homopolymer of EtOZO.

^d Calculated by N and Br (%) in the graft copolymer.

^e Determined by ¹H NMR spectroscopy.

^f [Grafted EtOZO(A value)]/[charged EtOZO] × 100.

precipitated copolymers (**4a** and **4b**) were separated and dried. The graft copolymer, *e.g.*, **4a-3** and **4a-4** thus obtained showed only one peak at around 70,000 in the GPC chart. Polymeric materials obtained from the THF-water solution, however, showed two peaks due to the homopolymer and graft copolymer. This reprecipitation procedure does not offer a complete separation method but was best among various combinations of solvents and non-solvents examined. Graft efficiency is generally not high, *i.e.*, up to 15.5% for the starting polymer **3a** (Table IV) and 50.0% for the starting polymer **3b** (Table V). This is mainly due to the loss of the graft copolymer during the above precipitation procedure which does not allow the complete separation of the graft copolymer and the homopolymer of MeOZO or EtOZO.

Graft copolymers, **4a** and **4b**, are basically the same in structure as examined by IR and ^1H NMR spectroscopy. The IR spectrum of the graft copolymers showed characteristic bands at 2920 and 2850 cm^{-1} (ν_{CH_2}), 1735 cm^{-1} ($\nu_{\text{C}=\text{O}}$ ester) and 1640 cm^{-1} ($\nu_{\text{C}=\text{O}}$ amide). The ^1H NMR spectrum (CDCl_3) of, *e.g.*, **4a-3**, showed a broad peak at δ 1.2 ppm due to methylene protons of the main chain overlapping with a triplet-like signal at δ 1.1 ppm due to methyl protons of ethyl group, a singlet at δ 2.0 ppm ascribable to methyl protons of acetate group, a broad quartet-like signal at δ 2.3 ppm due to methylene protons of ethyl group, a broad singlet at δ 3.5 ppm due to *N*-methylene protons, a broad peak at δ 4.2 ppm assigned to methylene protons between *N*-atom and carbonyl group of ester, and broad small signal at δ 4.8 ppm assigned to methyne protons. These spectral data confirm the structure of graft copolymer **4a-3**. From the integration ratio of *N*-methylene signal (δ 3.5 ppm) and methylene plus methyl signals (δ 1.2 and 1.1 ppm), the average graft chain length (grafted EtOZO mol/*X* mol) was 4.52 (*B* value in Table IV). This value is very close to that determined by elemental analysis (*A*

value = 4.13 in Table IV).

The average length of graft chain (*A* or *B* value) was obtained based on the assumption that initiation by **3a** or **3b** is fast in comparison with propagation. In fact the rate constants of initiation of EtOZO or MeOZO by a secondary alkyltosylate (**3a**) and by an alkyl bromide species (**3b**) are at least 10 times^{2c} and approximately 50 times²ⁱ smaller than those of propagation, respectively. Therefore, a small number of relatively long chains may have been grafted, especially in the case of tosylates **3a**.

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