

Preparation of Poly(butadiene-*g*-*N*-acetyleneimine) and Its Hydrolysis to Poly(butadiene-*g*-ethyleneimine)

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ABSTRACT: 2-Methyl-2-oxazoline (MeOZO) was polymerized by using 1-chloro-1,3-butadiene—butadiene copolymer as an initiator having reactive allylic chlorine. Polymerization was carried out in benzonitrile or in bulk. The active species of the MeOZO graft copolymerization was covalent-bonded alkyl chloride. The resulted graft copolymer was hydrolyzed under alkaline conditions to poly(butadiene-*g*-ethyleneimine). The structure of the graft copolymer was characterized by IR, NMR, as well as by an elemental analysis.

KEY WORDS Graft Copolymerization / 2-Methyl-2-oxazoline / 1-Chlorobutadiene—Butadiene Copolymer / Linear Polyethyleneimine / Alkyl Chloride Species / Alkaline Hydrolysis /

In a previous paper,¹ we described the synthesis of the ABA-type block copolymer of the linear polyethyleneimine (PEI) block (A) and the polybutadiene (PBD) block (B). The present paper describes the preparation of two graft copolymers whose parent polymer is a copolymer of butadiene with 1-chlorobutadiene (CBBR). One has a graft chain of poly(*N*-acetyleneimine), prepared by the graft copolymerization of 2-methyl-2-oxazoline (MeOZO) onto CBBR. The other consists of linear PEI branches and a CBBR main chain. This synthesis is based on our recent studies on the isomerization polymerization of MeOZO by alkyl chloride initiator.² In addition, recent papers by us describing the graft copolymerization of MeOZO onto chloromethylated polystyrene³ and on the hydrolysis of MeOZO polymer into linear PEI^{3,4} are cited. In the present study, CBBR⁵ was the parent polymer whose allylic halogen^{5,6} was utilized to initiate the MeOZO polymerization.

PEI is effective as a chelating polymer for heavy metal ions. Recently, we reported on chelating resin consisting of linear PEI and cross-linked polystyrene.³ In this paper we report on the preparation of an elastic chelating ion-exchange polymer using linear PEI, which is related to a chelating membrane prepared by the reaction of PEI

with polyepichlorohydrin.⁷

EXPERIMENTAL

Reagents

Commercial reagents of 2-methyl-2-oxazoline (MeOZO) and benzonitrile were dried and purified by distillation. Methanol, ethanol, chloroform, diethylether, and sodium hydroxide were commercial reagents and used without further purification.

Two samples of 1-chlorobutadiene—butadiene copolymer (CBBR) were prepared. The first one was a liquid polymer prepared by solution polymerization. A mixture of 2.0 g of 1-chlorobutadiene (CB), 28.5 g of butadiene, 111 ml of benzene and 0.32 g of α, α' -azobisisobutyronitrile was heated at 60°C for 44 hr. The product polymer was purified by reprecipitation (three times) from its benzene solution with methanol (nonsolvent), and dried *in vacuo* to give 3.42 g of CBBR. *Anal.* Found: C, 84.35; H, 10.43; Cl, 4.09. CB unit content was calculated from Cl content to be 6.38 mol%. The \bar{M}_n (by VPO) was 1,700. The second one was a higher molecular weight copolymer prepared by emulsion polymerization according to the literature.⁵ *Anal.* Found: C, 86.41; H, 10.93; Cl, 1.82. CB unit content was 2.84 mol%.

This polymer contained 0.76 mol% of 1-hydroxybutadiene unit because of the hydrolysis of the CB unit. $[\eta]=2.63$ (toluene, 25.9°C). The content of the hydroxylbutadiene unit was determined by a method using phenyl isocyanate.^{6,9}

Preparation of Poly(butadiene-g-N-acetyleneimine) (PBD-g-MeOZO)

The general procedure was as follows. Graft copolymerization was carried out in a glass tube under nitrogen. MeOZO was added to CBBR dissolved in benzonitrile. Then, the tube was sealed and heated at 100°C for 90 hr. In the case of bulk polymerization, CBBR was dissolved in MeOZO and the mixture was heated at 100°C for 40 h. After polymerization, methanol was added to the system to stop the reaction. The detailed reaction conditions are shown in Table I. The product was separated by extraction procedure shown in Figure 1.

Alkaline Hydrolysis of Graft Copolymer into Poly(butadiene-g-ethyleneimine) (PBD-g-EI)

NaOH (0.42 g, 10.5 mmol) was added to graft copolymer sample No. 1 (Fraction A, 0.43 g, MeOZO unit 4.24 mmol) in water (2 ml) and methanol (2 ml) containing 1% of 2, 6-di-*tert*-butyl-*p*-cresol. The mixture was stirred at 100°C for 40 hr in a sealed glass tube under nitrogen. The product mixture was filtered at about 90°C and the filtrate cooled. A white precipitate (linear polyethyleneimine) was isolated from the filtrate, washed with cold water, and dried *in vacuo* at 70°C to a constant weight of 0.11 g. The filtrate was dried and extracted with chloroform. The chloroform solution was poured into diethyl ether. The precipitated polymer (PBD-g-EI) was dried *in vacuo* to give 0.11 g of polymer. The chloroform insoluble part was 0.17 g.

Graft copolymer sample No. 3 (Fraction D, 3.78 g, MeOZO unit 11.38 mmol) was swollen in a mixed solvent of ethanol (15 ml) and water (15 ml). NaOH (3.78 g, 94.5 mmol) and 2, 6-di-*tert*-butyl-*p*-cresol (0.15 g) were added to the mixed solvent containing polymer. The mixture was heated at 100°C for 45 hr under nitrogen. After heating, the swollen polymer was isolated by filtration and washed with water until the washings became neutral. The polymeric material was dried *in vacuo* at 70°C to give 3.26 g of gel polymer. *Anal.*

Found: C, 80.40; H, 11.00; N, 4.39.

RESULTS AND DISCUSSION

Characterization of 1-Chloro-1, 3-butadiene Copolymer (CBBR)

Two kinds of CBBR were used. One was liquid rubber whose molecular weight was 1,700 (VPO). Its CB unit content was 6.38 mol%. It was reported that CBBR prepared by emulsion polymerization contains a small amount of hydroxyl group due to the hydrolysis of the CB unit.⁸ Since the liquid CBBR was prepared by solution polymerization (anhydrous system), the polymer had no hydroxyl group. The other CBBR was solid rubber ($[\eta]=2.63$ in toluene at 25.9°C) prepared by emulsion polymerization, CB unit 2.84 mol% and 1-hydroxybutadiene unit 0.76 mol%.

Preparation of Poly(butadiene-g-N-acetyleneimine) (PBD-g-MeOZO)

MeOZO was added to a benzonitrile solution of CBBR and the mixture was stirred at 100°C. In the case of liquid CBBR, bulk polymerization of MeOZO was also carried out. After the polymerization, separation of the polymer was carried out according to the procedure as described in Figure 1. The product was dissolved in methanol and the part insoluble in methanol was removed by filtration. The insoluble part was CBBR or the gel of the graft copolymer (Fraction D, Figure 1). The filtrate was not transparent, but milky, and was separated by centrifugation into a solid and a supernatant clear solution (Experiment No. 2). The supernatant liquid was poured into a large amount of diethyl ether and a white precipitate was obtained. It was identified as homopoly(*N*-acetyleneimine) (PMeOZO) (Fraction B, Figure 1) by comparing its NMR spectrum with that of an authentic sample of PMeOZO. The solid was dissolved in chloroform and reprecipitated with hexane. The reprecipitation procedure was repeated. The precipitated polymer contained a butadiene unit, whereas the hexane-soluble part contained no PBD. These findings indicate that the precipitated polymer consists of PBD-g-MeOZO (Fraction A, Figure 1) with or without being contaminated by homo-PMeOZO. When the solid part was not well separated by centrifugation (Experiment No. 1), the filtrate was

Preparation of Poly(butadiene-*g*-*N*-acetyylethyleneimine)

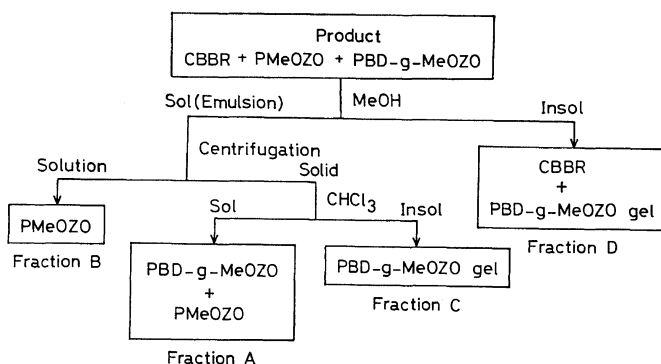


Figure 1. Separation procedure.

Table I. Graft copolymerization of MeOZO onto CBBR

No.	Reaction conditions						Fraction, % ^d		
	CBBR, g	MeOZO, g	PhCN, ml	Time ^a , h	Conversion, %	Total yield, g	A	B	C+D
1	0.51 ^b	1.5	4	90	79	1.70	92(77) ^e		8
2	0.47 ^b	1.5	0	40	98	1.94	58(57) ^e	40(100) ^e	2
3	3.98 ^c	25	60	90	12	6.95	0	25(100) ^e	75(18) ^e

^a At 100°C. ^b \bar{M}_n , 1,700; Cl, 1.15 mmol/g. ^c $[\eta]$, 2.63 (PhCH₃, 25.9°C); Cl, 0.52 mmol/g; OH, 0.14 mmol/g.

^d On the basis of the total polymer yield. ^e Analytical datum indicating the mole fraction (%) of PMeOZO in the respective fraction.

dried and the residue was dissolved in chloroform and reprecipitated with hexane. The unseparated homo-PMeOZO could be removed as linear PEI after hydrolysis of the graft copolymer (*vide infra*).

When high molecular weight CBBR was used as an initiator (Experiment No. 3), the soluble graft copolymer was not obtained, due to a crosslinking reaction of CBBR. The insoluble product was extracted with methanol to remove homo-PMeOZO, followed by the extraction with chloroform. The chloroform extract did not contain any CBBR. This means that all CBBR chains were cross-linked. The homo-PMeOZO was completely removed by extraction with chloroform. The results of the graft copolymerization are shown in Table I.

The IR spectrum of graft copolymer No. 1 (Figure 2b) showed absorption bands due to CBBR (911 and 967 cm⁻¹) and a strong band at 1620–1670 cm⁻¹ assignable to the amide $\nu_{C=O}$ of PMeOZO. The NMR spectrum of graft copolymer No. 1 (Figure 3b) showed absorption bands

due to CBBR and PMeOZO. The MeOZO unit content in the graft copolymers was determined from their NMR spectra and nitrogen content. The two calculations were in close agreement with each other. The MeOZO unit content in the gel graft copolymer was calculated on the basis of its elemental analysis.

The solubility and swelling properties of the graft copolymer depended on its PMeOZO content. The solubility of graft copolymer No. 1 containing 73 mol% of PMeOZO was similar to that of homo-PMeOZO. This is why the separation of homo-PMeOZO from the graft copolymer is rather difficult. Gel graft copolymer No. 3 was not well swollen in water or methanol, because it contained only 18% of MeOZO unit. Therefore, in order to remove homo-PMeOZO completely, it was necessary to extract the gel graft copolymer with chloroform in which both PMeOZO and CBBR were well soluble.

The polymerization of MeOZO by CBBR is considered to proceed according to the reaction

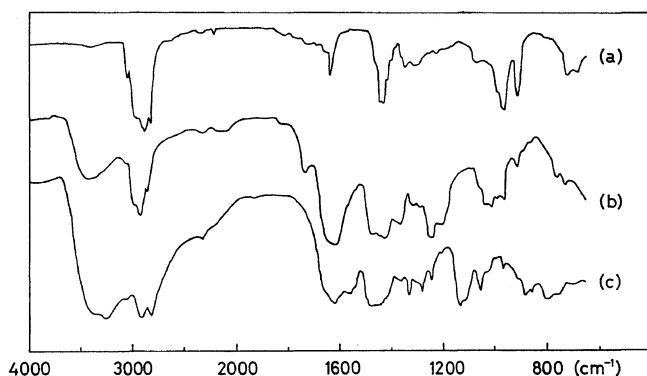


Figure 2. IR spectra of (a) CBBR, (b) PBD-g-MeOZO, and (c) PBD-g-EI.

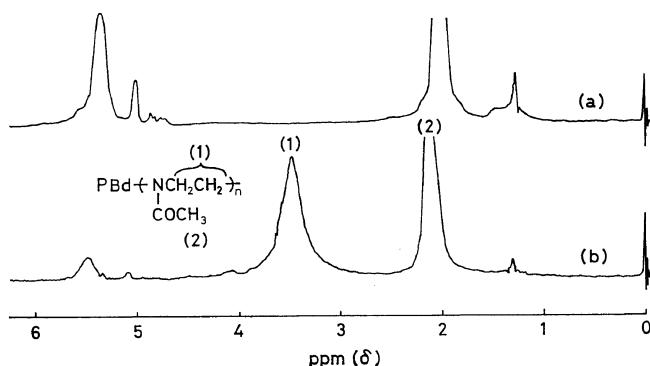
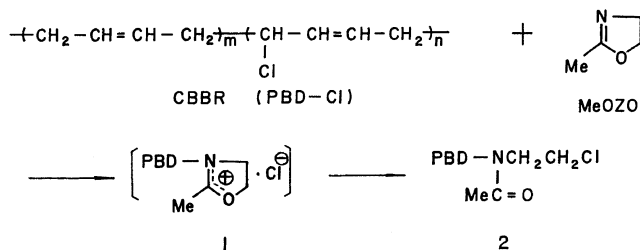


Figure 3. NMR spectra of (a) CBBR in CDCl_3 and (b) PBD-g-MeOZO in CDCl_3 .

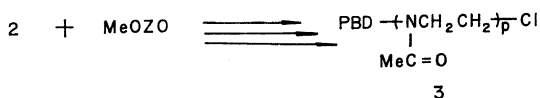
scheme proposed for the MeOZO polymerization initiated by benzyl chloride.² About 50–60% of CB unit is 1,4-linkage⁶ and its allylic chlorine is the active site for polymerization of MeOZO. Allyl chloride is one of the effective initiators of the polymerization of MeOZO; for example, 100% of conversion was obtained under the following

conditions: $[M]_0 = 3.69 \text{ mol/l}$, $[I]_0 = 0.47 \text{ mol/l}$, in CD_3CN at 100°C for 17 hr.¹⁰ In both the initiation and propagation, a polymer oxazolinium salt such as **1** is formed by bimolecular reaction of polymer alkyl chloride with MeOZO monomer. The intermediate species **1**, however, rearranges quickly to the covalent species **2** because of the

Initiation



Propagation

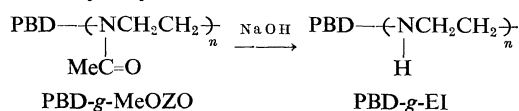


larger nucleophilic reactivity of Cl^- anion than that of MeOZO monomer. Therefore the propagating species of the MeOZO polymerization are covalent-bonded alkyl chloride species such as 2 and 3.

The formation of homopolymer of MeOZO during the graft copolymerization is due to the thermal degradation of CBBR producing HCl which initiates the homopolymerization of MeOZO. In addition, the possibility of the chain transfer to monomer cannot be excluded.¹¹ The degradation occurs at 147°C, and it occurs at lower temperatures in the presence of amines or acids.¹² In the graft copolymerization of MeOZO, the degradation possibly occurs under the experimental conditions because MeOZO monomer is basic.

Alkaline Hydrolysis of PBD-*g*-MeOZO to PBD-*g*-EI

PBD-*g*-MeOZO sample No. 1 was subjected to alkaline hydrolysis at 100°C for 40 hr. Most of the MeOZO unit (*e. g.*, 78.9%) was converted into the ethylenimine (EI) unit. The homo-PMeOZO contained in the sample was also hydrolyzed to linear PEI. Linear PEI is insoluble in cold water, whereas PBD-*g*-EI is soluble. Therefore, the separation of homo-PEI from the graft copolymer was relatively easy.



The IR spectrum of the hydrolyzed graft copoly-

mer (Figure 2c) has a weak amide group absorption band at 1630 cm^{-1} . Bands at 3260 cm^{-1} (NH) and 1130 cm^{-1} (C-N) are attributable to the linear PEI branch.⁴ The NMR spectrum of the graft copolymer (Figure 4a) shows peaks at δ 5.35, 5.02 and 2.03 ppm due to the protons of polybutadiene, and peaks at δ 2.69 and 2.12 ppm which are assignable to *N*-methylene protons and amine proton of PEI branch, respectively. The peak at δ 2.12 ppm decreased by treating the sample solution with D_2O (Figure 4b). Peaks at δ 3.43 and 2.03 ppm are also observed in Figures 4a and 4b, and are attributable to the protons of unhydrolyzed unit, *i. e.*, MeOZO unit. From the NMR spectrum, the degree of hydrolysis of the hydrolyzed graft copolymer was calculated to be 78.9%. The ratio of PBD/PEI/PMeOZO units was 27.3/57.3/15.4. The calculated value of \bar{M}_n from the above ratio is 5,800 and is in fair agreement with the experimental value, *i. e.*, 5,100 (VPO).

Gel PBD-*g*-MeOZO sample No. 3 was also subjected to alkaline hydrolysis. In this case no homo-PMeOZO was contained in the gel graft copolymer, since the homopolymer could be extracted completely with chloroform. The extent of the hydrolysis (%) and EI unit content (mmol/g) were determined by the difference between the nitrogen content of the starting and hydrolyzed graft copolymer. These were 30.6% and 0.96 mmol/g, respectively. These values correspond to PBD/PEI/PMeOZO=82.0/5.5/12.5. The lower extent of the hydrolysis is probably due to the fact that the graft copolymer does not swell in water very well. The adsorption capacity for Cu^{2+} ion

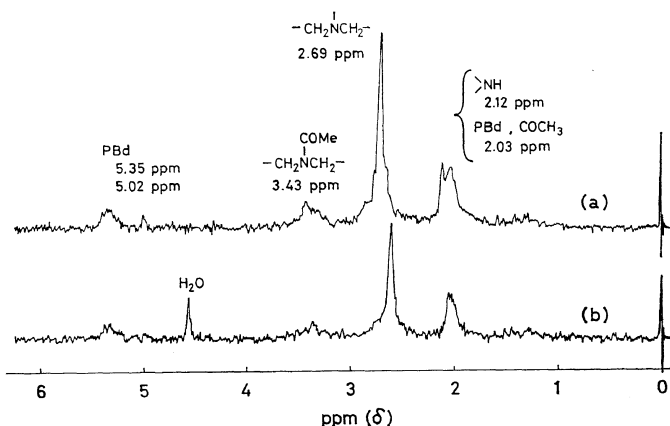


Figure 4. NMR spectra of (a) PBD-*g*-EI in CDCl_3 and (b) PBD-*g*-EI treated with D_2O in CDCl_3 .

of the gel graft copolymer was relatively small, *i. e.*, 0.08 mmol/g, because of its lower content of EI unit and its lower swelling capacity in water.

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