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Synthesis

Synthesis and morphology of poly(styrene-g-[propylene oxide-b-2-methyl-2-oxazoline])

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SUMMARY

Poly(styrene(ST)-g-[propylene oxide(PO)-b-2-methyl-2-oxazoline (MeOz)])s were prepared by ionic polymerization. Alkaline hydrolysis of these graft-block copolymers were carried out and poly(ST-g-[PO-b-ethylene imine(EI)])s were obtained. Morphologies of these copolymer specimens were obtained by electron microscope.

INTRODUCTION

Block and graft copolymers composed of incompatible block segments generally form a microdomain structure in the solid state as a consequence of microphase separation of the constituent block chains. We have reported the microphase separation of [ST-b-4-vinylpyridine(4VP)] copolymers and prepared the charge mosaic membrane by chemical modification(quartenization and sulfonation) of casting films accompanied with each domain fixing (1-4). The salt-enriched permeate with that membrane was about 20% (0.01N NaClaq, 650 psi.)(3). The charge mosaic membrane which consists three components (anion domain, cation domain, and insulator which works as electric insulator and stress-relaxation domain) is better than that composed of two components without insulator in strength and ion exchange capacity of the membrane. Fujimoto et al. synthesized penta-block copolymers which were applied to charge mosaic membrane(5).

On the other hand, we synthesized well-defined poly(ST-b-MeOz)(grass-crystalline) by ionic polymerization and studied its morphology(6-7).

In this article we selected PPO which has low Tg(-78°C) as an insulator and prepared poly(ST-g-[PO-b-MeOz]) and poly(ST-g-[PO-b-MeOz]) by ionic polymerization. Then we studied the morphologies of these copolymer specimens.

EXPERIMENTAL

Preparation of poly[ST-co-p-acetoxy styrene(AcST)]

Poly(ST-co-AcST) was prepared by radical copolymerization of ST with AcST (Maruzen Petrochemistry Co. Japan) initiated by α,α-azobisisobuthyronitrile in dioxane at 60-70°C using a sealed ampule. The fractionation of product was carried out by stepwise precipitation with the benzen-methanol system. Next, the acetoxy groups of poly(ST-co-AcST) were partially converted to phenoxyl group by alkaline hydrolysis with NaOHaq and dioxane. Remaining acetoxy groups was converted after grafting of phenoxyl groups by the second alkaline hydrolysis and used for crosslinking in the preparation of charge mosaic membrane.

Preparation of poly(ST-g-PO)

Phenoxyl group of poly(ST-co-AcST) was converted to sodium phenoxide groups as anionic initiating species(8). Sodium n-butoxide was added to tetrahydrofuran(THF) solution of poly(ST-co-AcST) at 60°C in vacuo. A small amount of N,N-dimethylformamide(DMF) was used in this work to dissolve the produced ion-complex. Anionic polymerization of PO was carried out at 60°C for 30-50 hours in vacuo. After polymerization the solution was poured into methanol-HClaq and washed well with water-methanol.

Preparation of poly(ST-g-[PO-b-MeOz]) and poly(ST-g-[PO-b-EI])

Tosylation of end hydroxy group of PPO, cationic polymerization with MeOz followed by alkaline hydrolysis of PMeOz sequence were described in preceding papers(6-7).

Characterization of polymers

The number-average moleculer weight($\overline{Mn}$) of poly(ST-co-AcST) were measured by gel permeation chromatography(GPC;Toyo Soda high-speed liquid chromatograph HLC-802A). GPC measurement was made in distilled THF at 38°C with a GMH column with a flow rate of 1.1 ml/min. Acetoxy group content was determined by NMR spectra in $CDCl_3$ (60MHz, Hitachi high-resolution NMR spectrometer R-24B) at $\delta 2.1$ (acetyl proton) and $\delta 6.8$-7.3 (aromatic proton). The compositions of poly(ST-g-PO) and poly(ST-g-[PO-b-MeOz]) were also determined by NMR in $CDCl_3$ at $\delta 6.8$-7.3(aromatic proton),$\delta 3.8$(methylene proton of PPO), and $\delta 2.1$(methyl proton of PMeOz). The degree of alkaline hydrolysis of PMeOz blocks was also determined by NMR spectra. The filtrate was evapolated to remove acetone, dioxane, and water. A known amount of 3-(trimethylsilyl)propane sulfonic acid, sodium salt as internal standard was added to the remaining solution. Acetyl proton of acetic acid sodium salt was determined by NMR in D_2O. Infrared(IR) spectra were taken on a Hitachi 285 grafting IR spectrophotometer.

Electron microscopy

Each graft-block copolymer (30mg) was dissolved in 3 ml of mixed solvent. The solvents were chloroform-methanol: 8/2 (vol/vol) for poly(ST-g-[PO-b-MeOz]) and aniline-DMF: 1/1 (vol/vol) for poly(St-g-[PO-b-EI]). A small amount of this solution was dropped on the copper mesh-plate and the solvent was allowed to evapolate slowly. These specimens were exposed to the vapor of osmium tetroxide. Morphological observation was made with a JEOL JEM-100CX electron microscopy.

RESULTS AND DISCUSSION

Synthesis of poly(ST-g-PO)

Figure 1 shows typical IR spectra of G4 series. In the

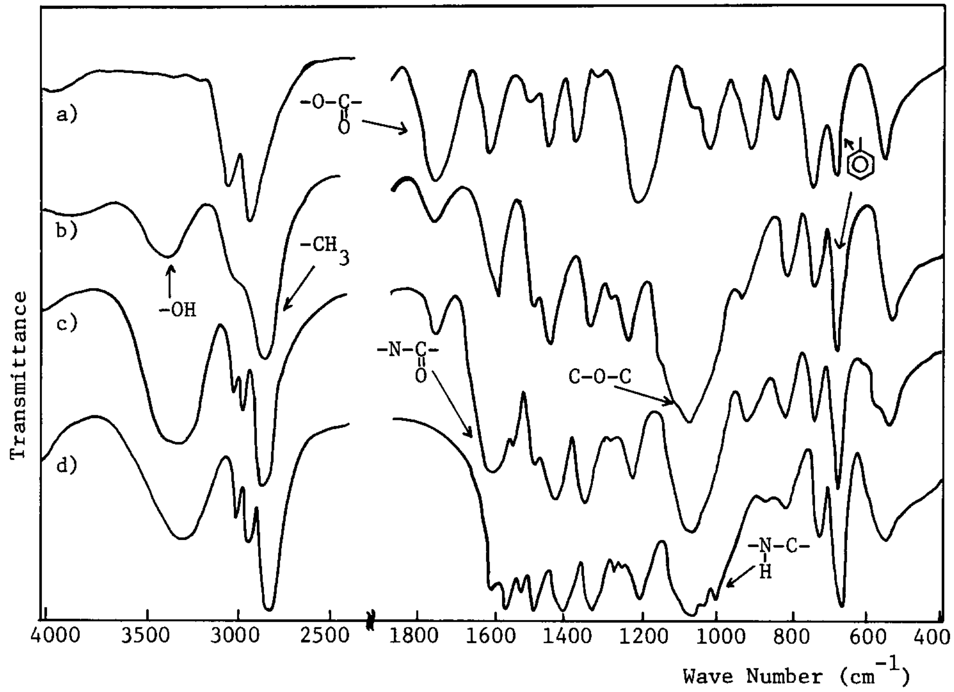


Figure 1 IR spectra of G4 series

a) poly(ST-co-AcST) b) poly(ST-g-PO)

c) poly(ST-g-[PO-b-MeOz]) d) poly(ST-g-[PO-b-EI])

Table 1 Polymerization Conditions and Results of poly(ST-g-PO)$^{a)}$

No	Feed			Yield (g)	$\overline{Mn}$ x 10^{-4}		PO / ST$^{e)}$ (mol/mol)
	Copolymer$^{b)}$ (g)	PO (ml)	n-BuONa$^{c)}$ (x10^3 mol) (calc.)		PST$^{d)}$	PPO$^{e)}$	
G1	3.0	9	5.0 (1.6)	3.0	48.0	3.0	0.13
G2	3.5	12	4.0 (1.5)	3.9	32.5	10.1	0.60
G3	1.0	7	2.5 (0.5)	1.4	7.3	1.0	0.27
G4	2.0	7	0.5 (1.1)	3.6	22.5	25.6	2.20
G5	0.9	7	0.5 (0.4)	1.2	51.0	12.8	1.00
G6	2.0	12	0.5 (0.9)	4.5	44.0	85.9	3.90

a) polymerized in vacuum at 60°C for 30-50hr, solvent: DMF(15-50ml)
b) poly(ST-co-AcST)
c) The value of parentheses show quantum of phenoxyl group of poly(ST-co-AcST).
d) by GPC e) by NMR

spectrum of G4(b), the broad absorption of ether bond at 1100 cm^{-1} appeared [cf. poly(ST-co-AcST)(a)]. In the NMR spectrum of G4, the peak which corresponded to methylene proton of PPO (δ=3.8) appeared. But the absorption of carbonyl(acetoxy group) at 1750 cm^{-1} in the IR spectrum and the resonance of acetyl proton (δ=2.1) in the NMR spectrum disappeared in all samples. According to these spectra, we could not synthesise the graft copolymer with protecting phenoxyl group by acetoxy group. This may be due to trans esterification of active end group with acetoxy group. Table 1 shows polymerization conditions and results of poly(ST-g-PO). The graft copolymers whose composition of PO/ST(mol/mol) was 0.1-3.9 were obtained.

Synthesis of poly(ST-g-[PO-b-MeOz])

Cationic polymerization with MeOz was carried out in DMF at 110°C. In the IR spectrum of BG4(c) in Figure 1, the broad absorption of amide group at 1650 cm^{-1} appeared, and in the NMR spectrum of BG4, the peak of methyl proton of PMeOz(δ=2.1) appeared. Table 2 shows results of cationic polymerization with MeOz. The highest conversion of MeOz was 74 % at BG4. But it seems that this polymerization was not living cationic polymerization and a deactivation occured. This deactivation is perhaps caused by the reaction between propagating speicis and remaining phenoxyl group.

Table 2 Cationic polymerization$^{a)}$with MeOz

No	Tosylated copolymer (g)		MeOz (ml)	conv. of MeOz (%)	PMeOz$^{b)}$ $\overline{Mn}$ x 10^{-4}
BG1	G1	1.0	2.0	29	28.0
BG2	G2	0.5	1.0	11	7.5
BG3	G3	0.9	1.5	63	8.6
BG6	G6	0.9	1.5	74	60.6

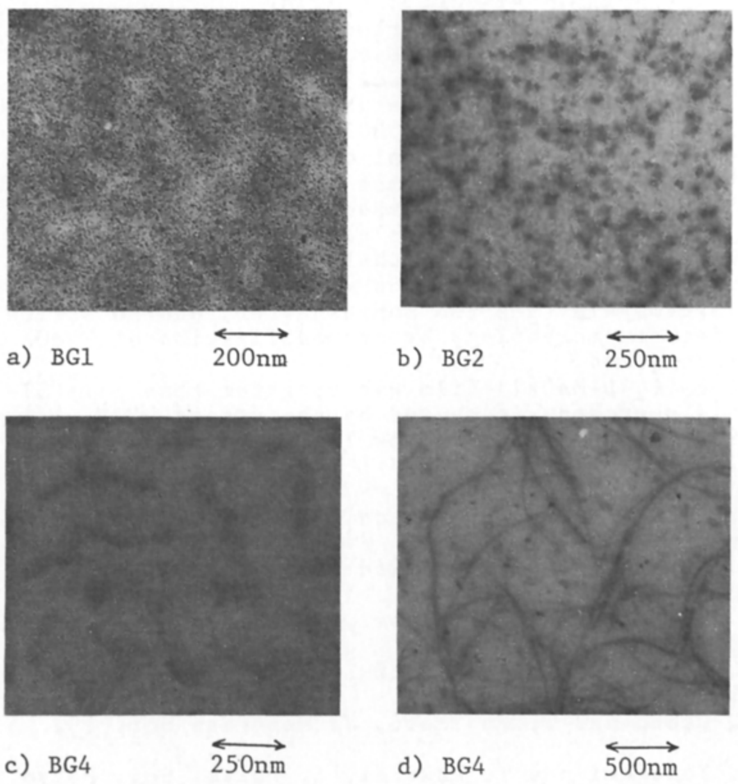
a) in vaccum at 110°C for 40 hr, solvent: DMF 1ml
b) by NMR

Synthesis of poly(ST-g-[PO-b-EI])

Alkaline hydrolysis of PMeOz sequences were carried out in dioxane-NaOHaq at 100°C for 40 hours. In the IR spectrum of EBG4(d) in Figure 1, the absorption of amide group at 1650 cm^{-1} disappeared and a new absorption of secondary amine group at 1050 cm^{-1} appeared. The degree of hydrolysis was about 60 %.

Morphology

We examined the morphology of poly(ST-g-[PO-b-MeOz]) and poly(ST-g-[PO-b-EI]) specimens, shown in Figure 2 in typical electron micrographs cast from chloroform-methanol(8:2vol) for poly(ST-g-[PO-b-MeOz]) and aniline-DMF(1:1vol) for poly(ST-g-[PO-b-EI]). The dark portions are the selectively stained PMeOz or PEI blocks. Table 3 describes the microdomain shape and domain size of poly(ST-g-[PO-b-MeOz])s and poly(ST-g-[PO-b-EI])s. Generally, the domain size of these copolymers was about half the size of poly(ST-b-4VP)(3) and poly(ST-b-MeOz)(7)'s domain size, which have same composition and molecular weight. It is caused by the structure of graft copolymer. In the case of applying to charge mosaic membrane with these materials, PPO



a) BG1 b) BG2 c) BG4 d) BG4

Figure 2. Electron Micrographs of Gragt, Block Copolymers from chloroform-methanol (8/2vol)

Table 3 Microdomain Shape and Domain Size of poly(ST-g-[PO-b-MeOz]) and poly(ST-g-[PO-b-EI]) specimens$^{a)}$

No	Composition (mol%)				Shape$^{b)}$	Domain Size$^{c)}$(nm)	
	PST	PPO	PMeOz	PEI		PST, PPO	PMeOz, PEI
BG1	52	7	41		L	40	50
BG2	69	12	19		S_{MeOz}	—	17
BG3	35	10	55		L, C_{MeOz}	29	31
BG4	15	33	52		L, C_{MeOz}	43	33
EBG1$^{d)}$	52	7	14	27	L, C_{MeOz}	50	50
EBG3$^{d)}$	35	10	23	32	L	28	33

a) Cast from chloroform-methanol(8:2vol)(BG series) or aniline-DMF(1:1vol)(EBG series)
b) L: Lamellar, C: Cylinder, S: Sphere
c) Sphere: the average domain diameter, Lamellar and Cylinder: the average domain distance
d) After alkaline hydrolysis

domain need not be very long in comparison with PST and PMeOz or PEI domains. In this view point, we compare two specimens (BG1, BG2: cast from chloroform-methanol) whose composition of PPO are about 10 mol% and molecular weight of PST are similar to each other. BG1(PMeOz 41 mol%) and BG2(PMeOz 19 mol%) specimens showed lamellar and spherical of PMeOz structures respectivily. Micrograph of BG4 specimen partially showed PMeOz fiblils(see (d) in Figure 2). As BG4 specimens had long chains of PMeOz, PMeOz sequences on copolymer partially crystallized and PMeOz fiblils were shown. The morphology after alkaline hydrolisis did not change in comparison with the morphology before alkaline hydrolysis (see EBG series(after) and BG series (before)). An effect to morphology by crystallization of PMeOz or PEI was not recognized.

The poly(ST-g-[PO-b-MeOz]) film was toughter than poly(ST-b-MeOz) film. This phenomena is caused by the stress-relaxiation of PPO domain which has low Tg(-78°C).

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