

Polysiloxane-Polyoxazoline IPN Gel의 제조 및 그 특성

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Polysiloxane-Polyoxazoline Interpenetrating Networks Gel : Preparation and Characterization

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요약 : 1,5-헥사디엔이 그래프트된 폴리실록산과 Si-H 함유 폴리실록산을 하이드로실화 하여 헥산과 톨루엔에 용매 팽윤성이 좋은 폴리실록산 겔을 얻었고 또 한편으로는 부분 가수분해된 폴리(2-메틸-2-옥사졸린)을 헥사메칠렌-디이소시아나이드와 우레탄 반응을 하여 폴리(옥사졸린) 겔을 얻었다. 아울러 양쪽 반응 시스템을 이용하여 동시 반응으로 상호 침투 구조의 겔을 제조하였다. 이때 양쪽 반응 모두는 각각의 촉매에 의해 영향을 받지 않았고 제조된 겔은 헥산/톨루엔과 물의 양쪽 성분에 모두 용매 팽윤성을 보였다. 또 DSC 열분석의 T_g 조사에 의해서는 블렌드 성질이 부분적으로 상용성이 있음을 알 수 있었다.

Abstract : Polysiloxane gel 6 was obtained from the hydrosilation between 1,5-hexadiene grafted polysiloxane 5 and polysiloxane 4 containing Si-H, which showed good swelling properties for organic solvents such as hexane and toluene. In addition, partially hydrolyzed poly(2-methyl-2-oxazoline) [poly(MeOZO)] 9 was prepared by the alkaline hydrolysis of amide group in poly(MeOZO) 8, which was used as raw materials, together with hexamethylene diisocyanate(HMDI) in the synthesis of poly(MeOZO) gel 7. Interpenetrating Network(IPNs) gel 10 was also obtained from the simultaneous interpenetrating crosslink reactions between 1,5-hexadiene grafted polysiloxane 5/polysiloxane 4 containing Si-H system and partially hydrolyzed poly(MeOZO) 9/HMDI system, where the cross influences to each reaction system by two catalysts were not observed. The gel having both hydrophobicity and hydrophilicity was confirmed from swelling properties for hexane/toluene and water, respectively. The blending properties between two polymer components were examined again by the varied glass transition points(T_g's) in DSC, which were observed to be partially compatible.

INTRODUCTION

Sada et al have already discussed that the nonionic hydrogel prepared from partially hydrolyzed poly(MeOZO) and HMDI can be used to obtain a range of hydrogels having varied water swelling capacity.¹ In many cases of hydrogels, the miscibilities to hydrophobic components such as polysiloxanes are very low. Therefore, it is very difficult to blend the components of hydrogels with those of polysiloxanes. If it possible, polysiloxane gels having organic solvent swelling will be able to provide hydrophobicities to nonionic hydrogels, while poly(MeOZO) gels having varied water swelling will be able to provide hydrophilicities to polysiloxane gels. As the result, the composite gel of new type obtained from these concepts will contain hydrophobicity as well as hydrophilicity in the gel. Consequently, in this paper, two immiscible polymer gels-one hydrophilic and the other hydrophobic-were combined to form IPNs system whose swelling properties for solvents could be varied by changing the compositions of hydrophilic and hydrophobic components. In spite of numerous hydrogels²⁻⁴ and organic gels,^{5,6} IPNs gel of this type have still not been synthesized due to the lack of compatibility and reactivity between two gels.

In relation to this study, the ladders of poly(dimethylorgano siloxane) (PDMS) using ethylene bridges as branch points were synthesized,⁷ and the sequential interpenetrating networks were prepared by mixing of hydroxyl- and short vinyl terminated PMDS.⁸ Recently, Martin Weber et al also reported the preparation of hydrophobic-hydrophilic two-component polymer networks using reactive poly(ethylene oxide) telechelics.⁸

This paper reports the preparation of polysiloxane gel by the hydrosilation between 1,5-hexadiene grafted polysiloxane and polysiloxane containing Si-H, poly(MeOZO) gel by the urethane reaction between partially hydrolyzed poly(MeOZO) and HMDI, and IPNs gel using simultaneous interpenetrating crosslink reactions between 1,5-hexadiene

grafted polysiloxane/polysiloxane containing Si-H system and partially hydrolyzed poly-(MeOZO)/HMDI system.

EXPERIMENTAL

Materials and Instruments : Octamethylcyclotetra siloxane(1), 1,3,5,7-tetramethylcyclotetra siloxane(2), hexamethyldisiloxane(3), HD, HMDI, CPA and ferric acetyl acetonate(FAA) were used without further purification. MeOZO, 1,8-diazabicyclo [5.4.0] unden-7(DBU), trifluoroacetic acid(TFA) and all solvents was dried and distilled under nitrogen atmosphere.

IR and H¹-NMR spectra were obtained with a Hitachi 250-60 and a Hitachi R-600(60MHz), respectively. The compositions of both graftmers and gels were calculated using a Youmoto MT-2 Elemental Analyser. Gel permeation chromatography(GPC) was carried out on a Simazu GC-6A after calibration with standard polystyrene samples. Molecular weights by vapor pressure osmometer (VPO) were determined in chloroform using a Hitachi 117 instrument. Glass transition point(T_g) was obtained using a Seiko SSS-5000 DSC fitted with a liquid nitrogen subambient accessory.

Solvent Swelling Property^{1,9}: Strips of the samples (~10~50mg) were immersed for 24hr in a large excess of solvent and then filtered using a glass filter(G-4) fitted with a aspirator (200mmHg) until the solvent on gel surface was removed. The degree of swelling was evaluated from the weight increase of solvent measured from the swelled gel based on dried gel. The measurements were performed at room temperature.

Polysiloxane Containing Si-H Bonds, 4 : As a typical example a mixture of 1 (10g : 33.7mmol), 2(0.26g : 1.07mmol), 3(0.08g : 0.5mmol) and TFA (0.11ml : 10mol% of Si-O bonds) was placed in a 30ml flask with a reflux condenser, and heated at 70°C for 64hr. The resulting viscous liquid was dissolved in a 25ml of dichloromethane as a best solvent for 4 and washed with distilled water repeatedly to remove the acid catalyst. Volatile

siloxane oligomers were removed by washing with methanol and evaporating under reduced pressure. The yield of colorless viscose liquid was 7.65g (74.4wt%).

The titration of Si-H bonds in 4 was carried out as follows¹⁰: 4 was reacted with mercuric acetate in $\text{CHCl}_3/\text{MeOH}$ (1/1, by vol). The evolved acetic acid was titrated with a MeOH solution of KOH using phenolphthalein as an indicator.

1,5-Hexadiene Grafted Polysiloxane, 5: In a 30ml flask, equipped with a reflux condenser, 4(Run 2) (0.91g), HD(0.07g : 0.85mmol) and CPA (0.017g : 0.043mmol) were stirred in a 1.2 ml of toluene/THF (3/1, by vol) at room temperature for 2hr, and then heated at 55°C for 55hr under nitrogen atmosphere. The CPA remained in the resulting solution was extracted by alumina, filtered and evaporated under reduced pressure to remove excess HD and solvents. The yield of colorless viscous liquid was 0.978g (~1-00wt%).

Polysiloxane Gel, 6: In a 30ml flask, 4 (Run 2) (0.80g), 5(Run 2) (0.80g) and CPA (0.015g : 0.037mmol) were stirred without solvent at room temperature for 24hr under nitrogen atmosphere. The resulting gel was extracted by soxhlet equipment using dichloromethane as a best solvent for 4 and 5. The amount of unreacted Si-H bonds in the gel was calculated by the above titration method, which was applicable to all samples. The yield of yellowish solid was 0.48g(30.3wt%).

Each hydrosilation for the preparations of 5 and 6 was carried out by the same procedure using a mixture of toluene and THF (3/1, by vol) in the presence of CPA : Toluene and THF were used as best solvents for each of 4/5 and CPA.

Poly(MeOZO) Gel, 7: In a 100ml flask, equipped with a reflux condenser, MeOZO (10g : 117.5mmol) and methyl tosylate (0.186g : 0.998mmol) were heated in a 50ml of acetonitrile at 75°C for 216hr under nitrogen atmosphere. The resulting slurry was separated as two parts of solid and solution,

where the only solution from the separation was evaporated, dissolved again in chloroform to remove the alkali catalyst, evaporated once more, washed with diethyl ether and dried. The yield of white solid 8 was 4.5g (44.9wt%). In addition, poly-(MeOZO) 8 (Run 1) (2.5g) was partially hydrolyzed at 95°C for 88hr in a 3ml of 0.1N NaOH diluted by a 100ml of water. The yield of partially hydrolyzed poly(MeOZO) 9 (Run 1) was 5mol%. In order to synthesize 7 (Run 1), 9 (Run 1) (0.14g) dried with benzene at freeze condition using dry ice under reduced pressure, HMDI (28.6μg : 0.017mmol) and DBU (25.9μg : 0.0154mmol) were added under nitrogen atmosphere, and stirred with a magnet bar at room temperature for 24hr. The resulting gel was extracted by soxhlet equipment using chloroform and methanol to remove the unreacted 9, HMDI and DBU, and dried under reduced pressure to remove the solvents. The yield of white solid 7 was 0.087g (62.2wt%).

The titration of N-H bonds in 9 was carried out as follows¹¹: 9 was titrated with a acetic acid solution of perchloric acid using methyl violet as an indicator.

Interpenetrating Networks Gel, 10: In a 30ml flask, 9 (Run 5) (0.112g) dried with benzene at freeze condition using dry ice under reduced pressure, 4 (Run 5) (0.063g), 5 (Run 2) (0.105g) and a mixture of HMDI (22.9μg : 0.0136mmol) and CPA (0.0021g : 0.0053mmol), DBU (19.2μg : 0.0076mmol) and FAA (17.1μg : 0.005mmol) were added under nitrogen atmosphere, and stirred with a magnet bar at room temperature for 24hr. The resulting gel was extracted by soxhlet equipment using chloroform, hexane and methanol to remove the unreacted 4, 5, 9, HMDI and catalysts, and dried under reduced pressure to remove the solvents. The yield of yellowish solid was 0.178g (63.7wt%).

RESULT AND DISCUSSION

A study on the preparation of 6 as shown in Table 1 have already been presented.¹² 6 was prepared by the procedures shown on Eq.(1). 8 was obtained by the cationic ring opening

Polysiloxane-Polyoxazoline IPN Gel

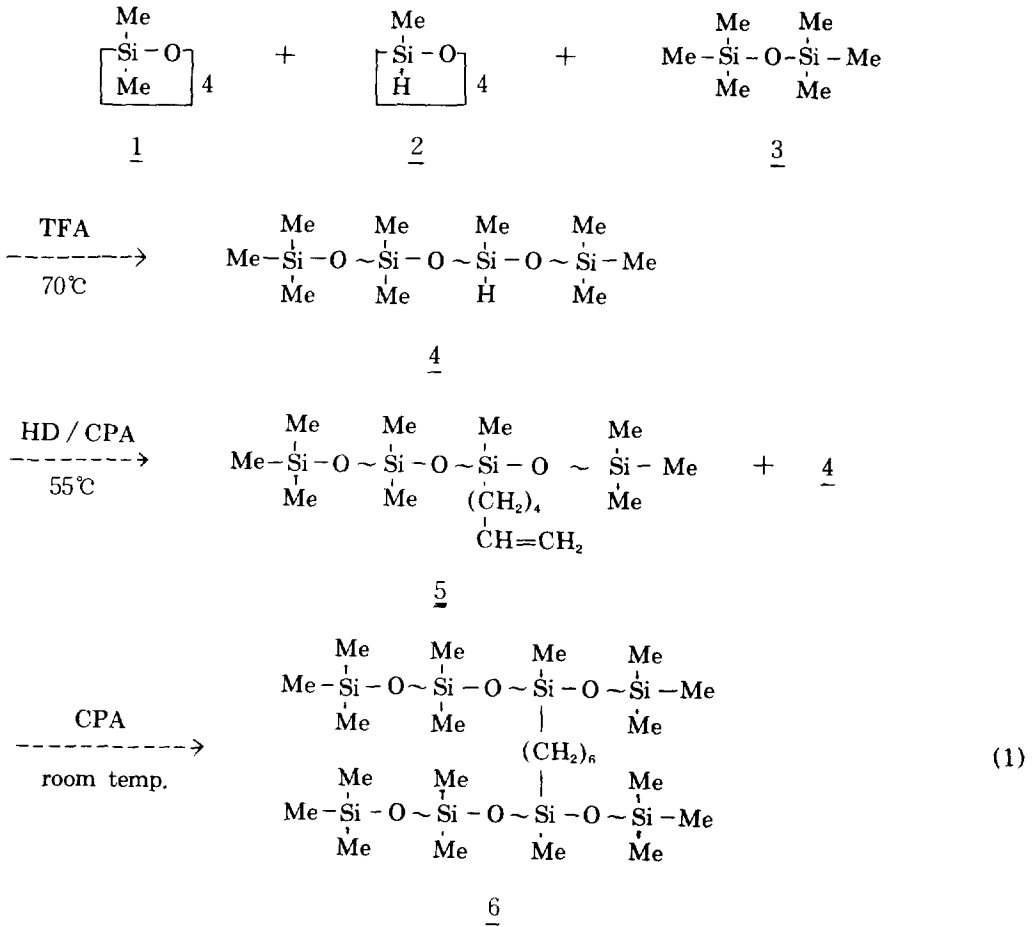


Table I. Preparation of Polysiloxane Gel(6)

Run	<u>4</u>				<u>5</u>			<u>5^b</u>	<u>6</u>			
	wt%(Si-H) ×10 ² tit.	Yield (%)	$\bar{M}_n \times 10^{-4}$ VPO	\bar{M}_w between c.lpts(Me)	wt% (C=C- C _n -) theor.	Yield ^a (%)	$\bar{M}_n \times 10^{-4}$ VPO	<u>4</u>	Yield(%) Examd.	Solvent Hexane	Swelling Toluene	(g/g) DMF
1	1.46	64.7	0.78	6800	1.23	100	0.78	1.0	none	none	none	none
2	2.41	74.4	0.85	4100	2.04	100	0.85	1.0	30.3	9.9	8.8	0.4
3	4.74	51.2	0.78	2100	4.10	100	0.92	1.0	40.2	5.7	5.3	none
4	6.71	53.3	0.83	1400	5.90	100	1.10	1.0	69.2	3.4	3.2	none
5	7.81	63.2	1.05	1200	6.93	100	1.75	1.0	81.3	2.4	2.1	none
6	5.39	48.8	0.37	1800	4.68	100	0.43	1.0	45.0	6.8	5.7	0.8
7	7.37	47.9	0.43	1300	6.52	100	0.45	1.0	57.9	3.1	2.6	none
8	7.81	63.2	1.05	1200	2.04	100	0.85	1.8	70.1	9.5	8.4	1.4
9	4.74	51.2	0.78	2100	2.04	100	0.85	1.4	62.3	7.6	7.1	0.8

^a: Measured value based on back titration of Si-H bonds.

^b: Weight feed ratio

Table 2. Preparation of Poly(2-methyl-2-oxazoline) (8)

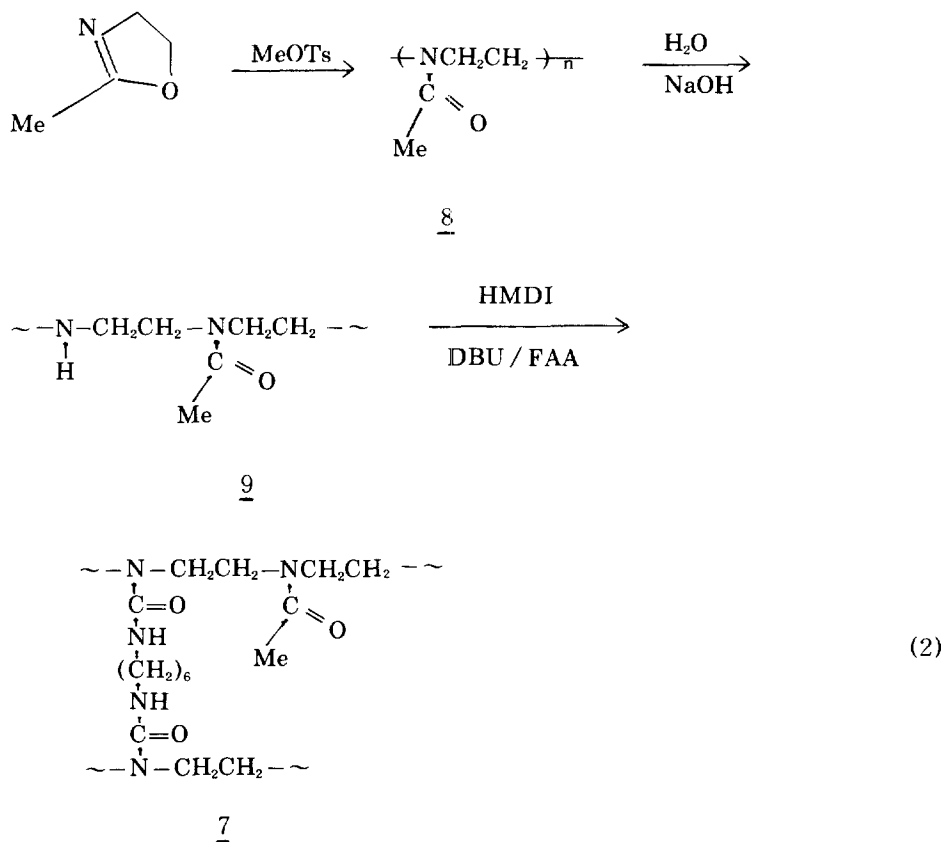
Run	[MeOZO] [MeOTs]	Temp. (°C)	Time (hr)	g		
				Yield(%) ^a	$\bar{M}_n \times 10^{-3}$ calc.	$\bar{M}_n \times 10^{-3}$ GPC
1	53.6	75	216	42.8	10.3	9.7
2	107.2	75	195	38.2	20.2	12.5

a : Soluble parts in DMF

Table 3. Preparation of Hydrolyzed Poly(2-methyl-2-oxazoline) (9)

Run	$\bar{M}_n^a \times 10^{-3}$ GPC	NaOH [NCOMe]	Temp. (°C)	Time (hr)	Hydrolysis (%)
					tit.
1	9.7	0.1	95	88	5.0
2	9.7	0.1	95	160	9.1
3	12.5	0.1	95	160	8.6

a : Mol. wt. of parent poly(MeOZO)



polymerization of MeOZO with methyl tosylate and the results are shown in Table 2. The molecular weight ranges of the reaction products were very broad, and a mixture of soluble and insoluble parts in acetonitrile was produced. Therefore, we selected the only soluble parts in acetonitrile in order to get homogeneous reaction products, where the soluble parts in acetonitrile were also soluble in DMF. DMF was used as a solvent

of 9 in gelation. 9 was prepared by a partial alkaline hydrolysis of amide group in 8. The results are summarized in Table 3. The conversion of hydrolysis in 9 could be controlled by both alkali concentration and reaction time. 7 was obtained from the crosslink reaction between 9 and HMDI in the presence of DBU in DMF as shown in Eq.(2). In particular, the reaction velocity and yield of 7 were much influenced

by the ratio of a mixture of 9 and HMDI to solvent as well as catalyst. In relation to this, when the amounts of solvent was above 3 times to that of the mixture, 7 was not obtained. The results are summarized in Table 4. 9 contains the units of N-acetylenimine(AEI) and ethylenimine(EI), and the units of EI in 9 are more available than those of AEI concerning water swelling property on 8 and increase with increase of hydrolysis. 7 had water swelling capacity up to 890wt% based on dried gel. The equilibrium water swelling property in 7 decreased with increase of crosslink points and AEI content and also increased with increase of molecular weight of 9. On the other hand, the possibilities of side reactions such as an intramolecular and a graft reaction by HMDI in the gelation between 9 and HMDI could not be examined: The ratio of HD to 9 in 7 was very low and the weight ratios of hydrogen, nitrogen and carbon contents in 9 were very similar to those of HMDI.

IPNs 10 consists of two inherently immiscible polymers: Polysiloxane 6 and poly(MeOZO) 7. The components in 10 are made by combining the linear polymers 4 and 9, together with crosslink agents such as 5 and HMDI. The reaction scheme should be the simultaneous combination of Eq. (1) and Eq. (2). It is of interest to synthesize both networks simultaneously. The basic requirement involves two independent, noninterfering reactions that can be simultaneously run over same conditions in the same container.¹³ At that time, both prepolymers have the gelation simultaneously. All of 10 made here was binary reaction

systems composed of a urethane reaction and a hydrosilation. In the reaction conditions, the crosslink influences to each reaction by two kind of catalysts were not observed, in which each crosslink reaction was possible to run over in the presense of catalysts of both sides. In addition to this, networks formation caused by the hydrosilation between 5 and HMDI as other side reaction did not take place at all in these experimental conditions.¹⁴ Here, as the speed of urethane reaction using the only DBU catalyst in the preparation of 10 was lower than that of hydrosilation using CPA as a catalyst, 10 was not obtained. Therefore, a mixture of DBU and FAA as cocatalyst was used to promote the reaction in the preparation of 10. Most reaction in 10 took place within 3hr, though the reaction time including post-curing was about 24hr. The IR spectra of 10 is shown in Fig. 1(C), where the characteristic bands of the two component polymers 6 and 7 are appeared. In order to remove the linear polymers in 10, 10 is purified by the extraction with chloroform which is a best solvent for 4/5 and 9. Two immiscible prepolymer with varied compositions are combined to form IPNs gel whose blending properties are examined by the survey of swelling properties for hydrophobic and hydrophilic two component solvents. Some of IPNs prepared simultaneously are apparently very compatible, although the reason is not well understood.¹⁵ But most of IPNs and related materials display phase separation characteristics, in which the phase domain size of the one of polymer is controlled by the crosslink density of the other polymer.

Table 4. Preparation of Poly(2-methyl-2-oxazoline) Gel (7)

Run	<u>9</u>			\bar{M}_w between c. l. pts(Mc)	<u>7</u>	
	$\bar{M}_n \times 10^{-3}$ GPC	-NCO -NH	Hydrolysis (%) tit.		Yield (%)	Water swelling (g/g)
1	9.7	0.68	5.0	2500	62.2	3.9
2	9.7	0.56	5.0	3000	54.2	5.2
3	9.7	0.31	9.1	3000	59.2	6.5
4	12.5	0.56	5.0	3000	62.2	5.6
5	12.5	0.33	8.6	3000	56.4	8.9
6	12.5	0.56	8.6	1800	66.2	6.4

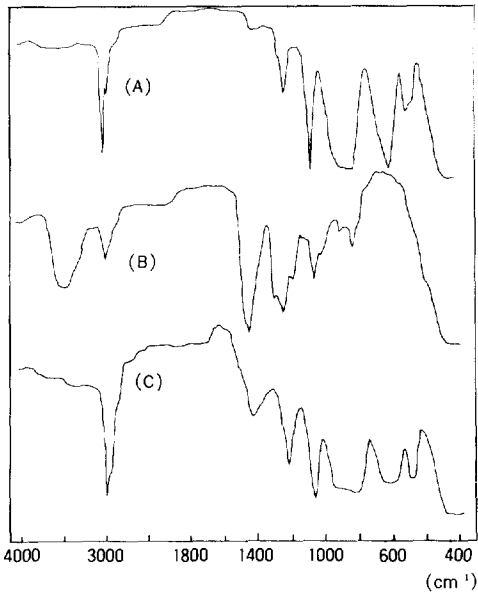


Fig. 1. IR spectra of (A) 6 (Run 2), (B) 7 (Run 3) and (C) 10 (Run 9).

¹⁶ In relation to these concepts, Table 5 shows the solvents swelling properties of 10 prepared with the varied compositions and crosslink agent contents. That is, there are several examples in the correlations of the swelling properties for hydrophobic and hydrophilic solvents such as hexane and water which are best solvents for 4/5 and 9, respectively. Here, we intend to explain the differences of solvents swelling properties between the IPNs gels and simple polyblend. As the results, the hexane swelling property in 10 was little influenced by the preparation method of IPNs.

In general, the characterization of 10 might be very difficult, because of very small variation in thermal and physical property such as T_g and crosslink density compared to those of general IPNs. But the change in thermal property in 10 as a function of the weight blend ratios of 4/5 to 9 was examined by DSC as shown in Fig. 2. Here, we used the accepted criterion that the increase or decrease of T_g was accompanied

Table 5. Preparation of Interpenetrating Networks Gel (10)

Run	<u>9</u>			<u>4 + 5^a</u>	<u>5^b</u>	<u>10</u>			
	Hydrolysis(%) tit.	-NCO	$\bar{M}_n \times 10^{-3}$ VPO	<u>9 + HMDI</u>	<u>4</u>	Yield(%)	<u>4 + 5</u>	Solvent Swelling(g/g)	
		-NH					<u>9 + HMDI</u>	Hexane	Water
1	5.0	0.68	9.7	6.77(1.89)	68.2	29.16	9.1(10.7) ^c	0.1(0.1)	
2	5.0	0.68	9.7	3.87(1.89)	56.6	4.90	6.9(9.8)	0.6(0.7)	
3	5.0	0.68	9.7	2.26(1.89)	38.2	1.51	5.6(6.6)	0.9(1.5)	
4	5.0	0.68	9.7	1.45(1.89)	49.3	1.39	4.4(6.3)	1.0(1.6)	
5	5.0	0.68	9.7	0.65(1.89)	63.7	0.67	3.3(4.3)	1.4(2.3)	
6	8.6	0.33	12.5	3.91(1.89)	48.7	6.26	9.0(9.5)	0.8(1.2)	
7	8.6	0.33	12.5	1.47(1.89)	55.8	4.87	8.3(9.1)	1.2(1.5)	
8	8.6	0.33	12.5	0.65(1.89)	61.1	0.77	4.1(4.5)	3.6(5.0)	
9	5.0	0.56	12.5	3.91(1.89)	59.3	7.20	8.4(9.8)	0.4(0.8)	
10	5.0	0.56	12.5	1.47(1.89)	37.2	3.85	6.0(8.8)	1.0(1.4)	
11	-	-	-	- (1.89)	72.1	-	11.1	none	
12	5.0	0.68	9.7	-	62.2	-	none	3.9	
13	5.0	0.56	12.5	-	62.2	-	none	6.6	
14	8.6	0.33	12.5	-	56.4	-	none	8.9	

a, b : Weight feed ratio

4 : wt%(Si-H) $\times 10^2$ tit.: 7.81, $M_n \times 10^{-4}$: 1.75

5 : wt%(C=C-C₄-) $\times 10^2$ tit.: 2.04, $M_n \times 10^{-4}$: 0.85

c : Reduced swelling property based on each polymer components in 10

Run 11~14 : 6 or 7

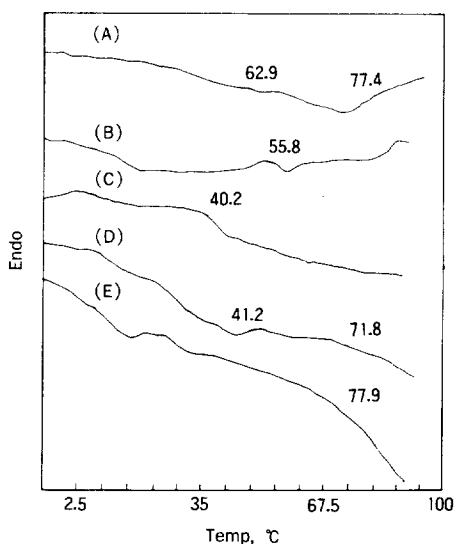


Fig. 2. DSC thermograms of interpenetrating network gel : (A) 1:1 weight blend of 4 to 9, (B) 10 (Run 8), (C) 10 (Run 10), (D) 10 (Run 5), (E) 7 (Run 1).

for the polymer-polymer miscibility.¹⁷

T_g of 10 obtained from a MeOZO side was as same as that of 8 or 9, because the effect of crosslink by HMDI in 10 was very small. In addition, the data in Fig. 2(A) indicates that the 1:1 weight blend of 4 to 9 do not show the decrease of T_g in a MeOZO side, which stands for the existence of immiscibility between two component polymers. Therefore, if there is a variation of T_g in 10, 10 can be verified as IPNs gel. As the results, most of T_g 's in 10 brought about some decrease comparing to that of 9, but gradually decreased with increase contents of 9 in 10. Each component (4/5 and 9) in 10 was found to be ununiformly distributed from the results of T_g measurements, taking into account the existence of one T_g in a compatible polyblend. That is, 10 was regarded as chemical blending with partial compatibility. Consequently, it meant that the hexane swelling properties of 10 considerably decreased with increase of the content of MeOZO, and increased with increase of the content of siloxane. On the contrary, the water swelling

properties of 10 gradually increased with increase of the content of MeOZO, and decreased with increase of the content of siloxane. On the other hand, the decrease of swelling properties for both solvents was caused by the increase of the content of crosslink agent in 10 in all cases. Solvents swelling properties of 10 made here are smaller than that of each homo gel based on equivalent contents, which can be explained as the correlation by little increase of crosslink density in 10. In particular, the differences of solvents swelling properties in the polyblend of two immiscible homo gels such as 6 and 7 are not showed, which also meant the absence of interfering phenomena caused by polymer-polymer interactions between two immiscible polymer systems used here.

CONCLUSIONS

Novel polysiloxane gel having good swelling properties for organic solvents such as hexane and toluene was synthesized. In relation to this, polyoxazoline having higher water swelling property as a component of counter part to the polysiloxane was introduced to the preparation of the composite gel between two contrastive polymer components. Interpenetrating networks gel made here was newly rationalized as solvents swelling properties caused by the effect of the hydrophobic / hydrophilic balance in the gel.

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