

Graft Copolymerization of *N*-Isopropylacrylamide on Styrene-Butadiene-Styrene Block Copolymer

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ABSTRACT: Graft polymerization of *N*-isopropylacrylamide (NIPAAm) onto styrene-butadiene-styrene (SBS) block copolymer using benzoyl peroxide was studied to improve the water absorptivity and thermosensitivity of SBS. The influence of various grafting reaction factors on the conversion of NIPAAm and the grafting percentage of SBS-*g*-NIPAAm were also investigated in the study. The experimental results showed that the conversion of SBS-*g*-NIPAAm was enhanced as the monomers of NIPAAm were increased. The maximum conversion of SBS-*g*-NIPAAm was observed when the molar ratio of NIPAAm to butadiene was 1.25. In addition, increasing the reaction time enhanced the conversion of SBS-*g*-NIPAAm; the maximum grafting percentage was obtained with a 4-h reaction. The optimal concentration of the initiator was 3×10^{-4} mol/20 mL of toluene, and the grafting reaction occurred at over 65°C. The test results of the hydrophilicity of the grafted membranes showed that the hydrophilicity and thermosensitivity were significantly enhanced by grafting NIPAAm onto SBS. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2641–2650, 2001

Key words: styrene-butadiene-styrene; *N*-isopropylacrylamide; grafting copolymerization; thermosensitivity

INTRODUCTION

Styrene-butadiene-styrene (SBS) block copolymer, a microphase separated polymer with excellent mechanical properties^{1,2} and comprising glassy and rubbery microdomains, is used as a thermoplastic elastomer. It behaves as a vulcanized rubber at room temperature and can be processed as a thermoplastic at an elevated temperature. As a result, such copolymers have gained considerable attention in recent years. In industrial applications, SBS is used for the rubber soles of shoes. Even though polymeric materials have been widely used for their desirable

properties such as flexibility, viscosity, resistance to organic materials, impact resistance, and so forth, further modifications of the polymeric properties by various methods have been extensively studied to improve the inherent properties.^{3–22} Of these, graft polymerization is a well-known method for the modification of the chemical and physical structures to tailor properties for a specific application. This polymerization achieves specifically designed polymer properties by connecting different types of polymers with the desired properties in the same polymer chain. The typical method of graft polymerization is a radical polymerization of various monomers that is initiated by a chemical initiator,^{23–30} plasma,^{31–36} electromagnetism, γ -ray irradiation,^{9–15,37–41} and UV photografting.^{16–22}

In a previous study⁴² dimethylaminoethyl methacrylate (DMAEMA) was grafted onto a

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SBS copolymer membrane by the UV irradiation method; the solubility of oxygen in the SBS-*g*-DMAEMA membrane increased with the increase of DMAEMA grafting. 2-Hydroxyethyl methacrylate (HEMA) was also grafted onto a membrane of SBS by a γ -ray irradiation method.⁹ The mechanical properties of SBS-*g*-HEMA were found to be superior to those of poly(HEMA) and were identical with those of SBS, and the wetting and nonthrombogenic properties of SBS-*g*-HEMA were both better than those of SBS. The graft polymerization method for blood compatibility was also studied,^{43,44} and the blood compatibility of a modified SBS was measured by the Lee-White clotting test.^{9,14} Numerous investigators found that foreign surfaces rapidly adsorb plasma proteins when exposed to blood,⁴⁵ so it is essential to have an understanding of protein-polymer interaction for the development of antithrombogenic material. Side-chain liquid crystalline polymers (SCLCPs) were grafted to SBS by radical polymerization.⁴⁶ The results indicated that the SBS-*g*-SCLCPs samples exhibited much improved properties compared to the solution-cast blends. The improvement was mainly characterized by a much stronger mechanical strength, an essentially homogeneous morphology with the liquid crystalline component uniformly dispersed, and an enlarged liquid crystalline phase in some cases.

Poly(*N*-isopropylacrylamide) (PNIPAAm) exhibits a lower critical solution temperature (LCST) at around 32°C in aqueous solution, which is well known. The water contents of such polymer gels rapidly decrease when the temperature is above the LCST. The characteristics of the PNIPAAm gel were applied to prepare temperature-responsive gels and absorbents.⁴⁷⁻⁵⁰

The graft copolymerization of NIPAAm onto SBS using benzoyl peroxide (BPO) as an initiator was studied to provide hydrophilicity and thermosensitivity to the SBS. The influence of various grafting reaction factors on the conversion of NIPAAm and the grafting percentage of SBS-*g*-NIPAAm were also investigated.

EXPERIMENTAL

Materials

The SBS (Kraton® D-1101, Shell Co. Ltd.) was used as received, and its characteristics are listed in Table I. The NIPAAm (Wako Pure Chemical

Table I Physical Properties of Kraton® D-1101

Butadiene/styrene ratio (wt %)	69/31
Total molecular weight	1.02×10^5
Microstructure of PB	
1,4- <i>trans</i> (%)	42
1,4- <i>cis</i> (%)	49
1,2 (%)	9
Specific gravity	0.94
Viscosity at 25°C and 25% toluene (CP)	4000
Melt flow at 180/5 kg (g/10 min)	<1.0
ASTM D412	
300% Modulus (MPa)	2.9
Tensile strength (MPa)	33.0
Elongation (%)	880
Hardness, type A	72

Co. Ltd.) was further purified by recrystallization. The BPO was recrystallized by dissolving it in chloroform at room temperature and then precipitating by methanol. Toluene, *n*-hexane, methanol, and cyclohexane were used as received.

Graft Copolymerization of SBS-*g*-NIPAAm

The reaction conditions of the graft copolymerization of SBS with NIPAAm are shown in Table II. First the SBS and toluene solvent (20 mL) were stirred for complete dissolution; the solution was then heated to 50°C under a nitrogen atmosphere. When the desired temperature was reached, the NIPAAm monomer (a known amount containing BPO) was added with stirring. The reaction was carried out for predetermined periods. The mixture was then cooled and poured into an excess of well-stirred *n*-hexane. The precipitated polymer was filtered and washed several times with *n*-hexane and then dried to a constant weight at 50°C under a vacuum. The precipitate was a mixture of SBS-*g*-NIPAAm grafted copolymer, PNIPAAm, SBS, and crosslinked SBS.

Separation

The solubilities of SBS, PNIPAAm, and SBS-*g*-NIPAAm are shown in Table III, and the separation process is shown in Scheme 1. The PNIPAAm was removed first by a Soxhlet extractor with methanol as a solvent. The SBS was then removed with cyclohexane as a solvent. In the final steps the mixture was dissolved in 1,4-dioxane, the insoluble crosslinked SBS was filtered from the solution, the filtrate was poured into a petri dish, and the solvent was vaporized. The remain-

Table II Reaction Conditions of SBS-*g*-NIPAAm Grafting Reaction

Sample No.	SBS (g)	NIPAAm ($\times 0.013$ mol)	BPO ($\times 10^{-4}$ mol)	Reaction Time (h)	Reaction Temp. ($^{\circ}\text{C}$)
A1 (1 : 0.75)		0.75			
A2 (1 : 1)		1			
A3 (1 : 1.25)		1.25			
A4 (1 : 1.5)	1	1.5	1	4	75
A5 (1 : 2)		2			
A6 (1 : 2.5)		2.5			
A7 (1 : 2.75)		2.75			
B1 (0.75 : 1)	0.75				
B2 (0.875 : 1)	0.875				
B3 (1 : 1)	1				
B4 (1.25 : 1)	1.25	1	1	4	75
B5 (1.5 : 1)	1.5				
B6 (2 : 1)	2				
C1 (1 h)				1	
C2 (2 h)				2	
C3 (3 h)	1	1	1	3	75
C4 (4 h)				4	
C5 (6 h)				6	
D1 (0.8)			0.8		
D2 (1)			1		
D3 (2)			2		
D4 (3)	1	1	3	3	75
D5 (4)			4		
D6 (7)			7		
D7 (10)			10		
F1 (65 $^{\circ}\text{C}$)					65
F2 (70 $^{\circ}\text{C}$)					70
F3 (75 $^{\circ}\text{C}$)	1	1	1	3	75
F4 (80 $^{\circ}\text{C}$)					80
F5 (85 $^{\circ}\text{C}$)					85
F6 (90 $^{\circ}\text{C}$)					90

ing SBS-*g*-NIPAAm membrane was dried under a vacuum and weighed.

Measurement of Grafting Parameters

The grafting parameters were estimated from the weight of the sample before and after grafting. The percentage of grafting and the grafting efficiency (GE) were calculated according to the following relationships:

% grafting

$$= \frac{\text{mass of NIPAAm in SBS-}g\text{-NIPAAm}}{\text{mass of SBS-}g\text{-NIPAAm}} \times 100\% \quad (1)$$

$$\text{GE} = \frac{\text{mass of NIPAAm in SBS-}g\text{-NIPAAm}}{\text{mass of NIPAAm in SBS-}g\text{-NIPAAm} + \text{mass of PNIPAAm}} \times 100 \quad (2)$$

Characterization Techniques

The IR spectra of the casting films were measured on a spectrophotometer (Horiba FT-7X0) in the range of 400–4000 cm^{-1} .

Water Content Measurement

The water contents of the SBS-*g*-NIPAAm membranes were tested by immersing the dry weighed membranes (W_d) in deionized water at various temperatures. The weight of a wet sample (W_w)

Table III Solubilities of SBS, PNIPAAm, and SBS-*g*-NIPAAm

Solvent	PNIPAAm	SBS	Mixture	SBS- <i>g</i> -NIPAAm (GR = 23.8)
Water	○	×	×	×
Methanol	○	×	×	×
Ethanol	○	×	×	×
Isopropanol	○	×	×	×
Acetone	○	△	△	×
MEK	○	△	○	○
MIBK	△	○	○	○
Cyclohexanone	○	○	○	○
Cyclohexane	×	○	△	×
n-Hexane	×	S	×	×
1,4-Dioxane	○	○	○	○
DMAc	○	△	×	×
DMF	○	△	×	×
DMSO	○	×	○	×
Acetonitrile	○	×	×	×
Chloroform	○	○	○	○
Ethyl Acetate	○	△	○	○
Petroleum ether	×	S	×	×
Benzene	×	○	○	△
Toluene	×	○	○	△
Xylene	×	○	○	△

(○) soluble, (△) slightly soluble, (×) insoluble, and (S) swelling.

was determined after removing the surface water by blotting with filter paper at various time intervals until absorption equilibrium was attained. The water content based on W_w and W_d was then calculated as follows:

$$\text{water content} = (W_w - W_d)/W_w \quad (3)$$

RESULTS AND DISCUSSION

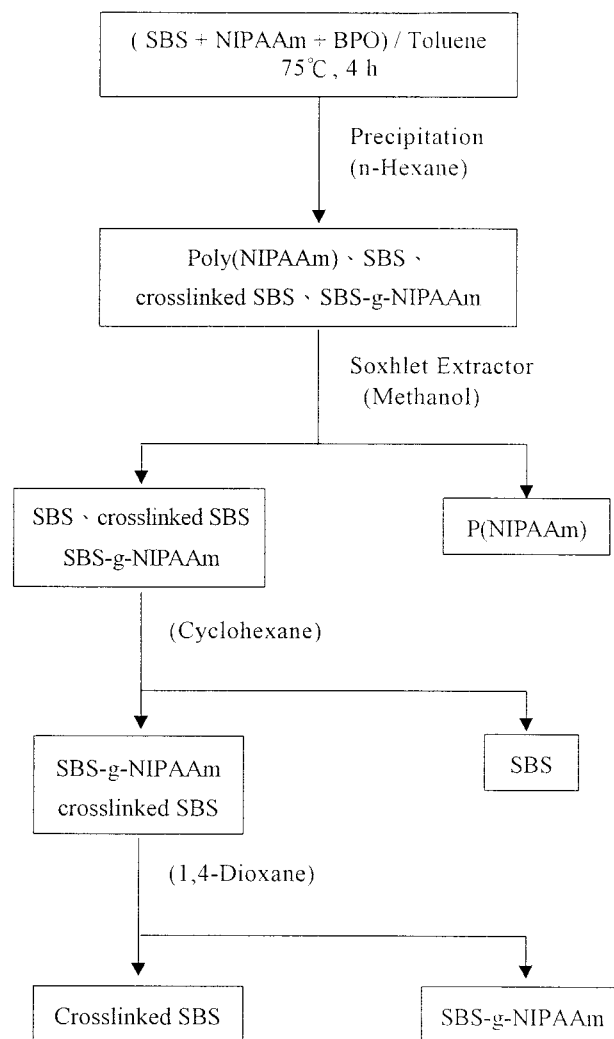
Characterization of SBS-*g*-NIPAAm Graft Copolymer

The use of IR spectroscopy is a well-known method for the identification of functional groups and quantitative analysis. The IR spectra of SBS, PNIPAAm, and the graft copolymers are exhibited in Figure 1. The appearance of new peaks in the grafted sample at 1716 cm^{-1} indicated the addition of the carbonyl group and at 3284 cm^{-1} indicated the addition of the secondary amine group of NIPAAm.

Effect of NIPAAm/Butadiene Molar Ratio on NIPAAm Conversion and Grafting Percentage

There is 0.013 mol of butadiene in 1 g of SBS. Figure 2 and Table IV show the effect of the molar

ratio of NIPAAm/butadiene in 20 mL of toluene (range of 0.75–2.75) on the conversion, grafting efficiency, and grafting percentage. The percentage of grafting of NIPAAm increased gradually with an increasing molar ratio of NIPAAm/butadiene in 20 mL of toluene (0–1.25). The percentage of grafting was 10.4% when the molar ratio of NIPAAm/butadiene was 0.75. Furthermore, it reached a maximum value of 24.4% when the molar ratio of NIPAAm/butadiene increased to 1.25. Beyond this molar ratio, the percentage of grafting was constant when the molar ratio of NIPAAm/butadiene increased. This result was similar to outcomes reported by Saroop and co-workers⁵¹ and our previous studies.^{52–54} This was because the grafted chains generally grew until the active sites were completely occupied and reached a maximum grafting percentage. Above this molar ratio (1.25) the excess NIPAAm monomer generated a large amount of PNIPAAm homopolymer (see Table IV, C_h). This event resulted in reducing the grafting efficiency. This result shown in Table IV for the conversion of NIPAAm for the overall polymerization (C_p), grafting copolymerization (C_g), and homopolymerization (C_h) was also confirmed by the results under polymerization conditions.



Scheme 1 The separation process.

Effect of SBS Concentration on Grafting Percentage

The effect of the concentration of SBS in the range from 0.75 to 2 g/20 mL of toluene on the conversion, grafting efficiency, and grafting percentage is shown in Figure 3 and Table V. The percentage of grafting was gradually increased with the increase of the concentration of SBS from 0 to 0.875 g/20 mL of toluene. The percentage of grafting was 12.2% when the SBS concentration was 0.75 g/20 mL of toluene. Furthermore, it reached a maximum value of 23.8% when the SBS concentration was increased to 0.875 g. Beyond this concentration (1 g/20 mL of toluene), the percentage of grafting and the grafting efficiency were decreased with an increasing concentration of SBS. This was because the viscosity of the SBS in tol-

uene interfered with the grafting reaction. This result can also be seen from Table V. The conversion of NIPAAm for C_p , C_g , and C_h decreased conspicuously with the increase of the concentration of SBS. This event can be attributed to the solution becoming more viscous when the SBS concentration was increased. A large amount of NIPAAm homopolymer was then formed and it decreased the percentage of grafting and the grafting efficiency. This phenomenon was also observed in previous studies.^{52,54}

Effect of Reaction Time on Grafting Percentage

The effect of the reaction time (1–6 h) on the conversion, grafting efficiency, and grafting percentage is shown in Figure 4 and Table VI. The percentage of grafting gradually increased with increasing the reaction time from 1 to 4 h. The percentage of grafting was 3.8% when the reaction time was 1 h. It reached a maximum value of 23.1% when the reaction time was increased to 4 h. Beyond 4 h the percentage of grafting and the grafting efficiency slightly decreased with increasing reaction time to 6 h. This meant that the grafted chains generally grew until the active sites were occupied completely and reached maximum grafting at a particular time, after which the grafting percentage and the grafting efficiency did not increase. From the results shown in Table VI, the C_g increased continuously with the increase of the reaction time but did not increase at 6 h. This result was different from the results obtained from HEMA grafted onto dehydrochlorinated poly(vinyl chloride) (DHPVC).⁵² However, it was quite similar to the results obtained from NIPAAm grafted onto DHPVC⁵⁴ and AAm grafted onto poly(hydroxybutyrate-co-hydroxyvalerate) film.⁵⁵

Effect of Initiator Concentration on Grafting Percentage

The effect of an initiator concentration range of $(0.8-10) \times 10^{-4}$ mol on the conversion, grafting efficiency, and grafting percentage is shown in Figure 5 and Table VII. The percentage of grafting and grafting efficiency were slightly increased with the increasing of the initiator concentration from $(0.8$ to $2) \times 10^{-4}$ mol, and then they increased to a maximum with the increasing of the initiator concentration to 3×10^{-4} mol. This was due to the increasing chance of hydrogen abstraction from the backbone and the chain transfer

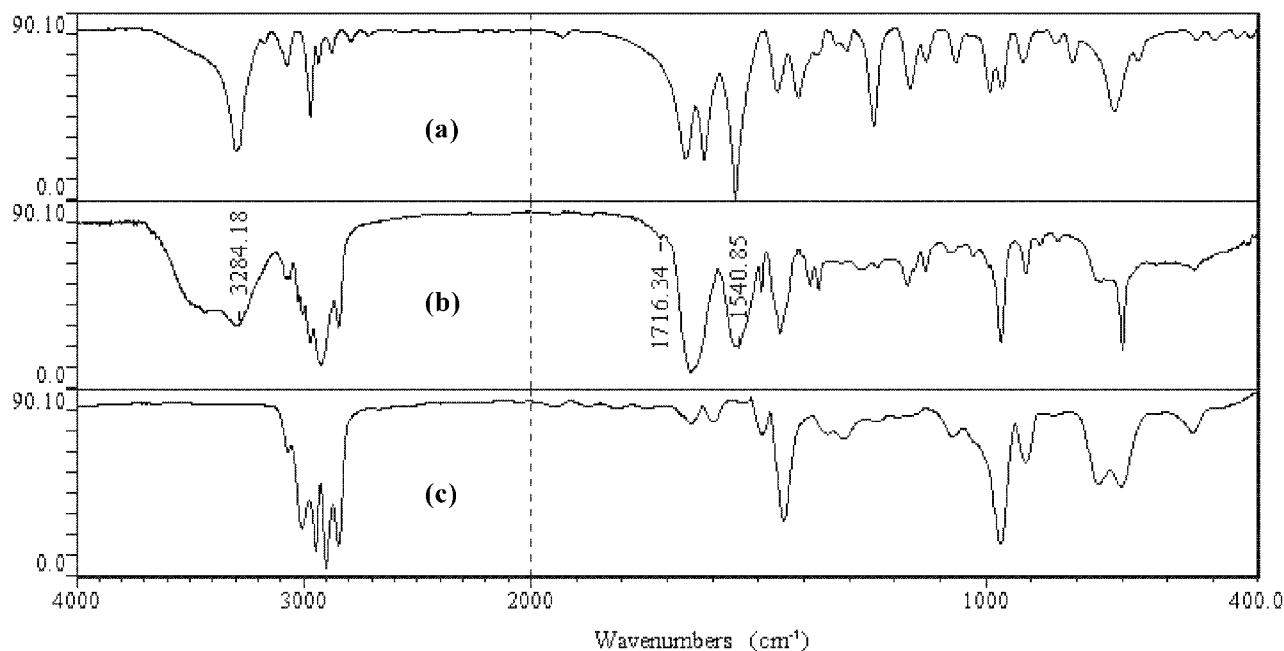


Figure 1 IR spectra of PNIPAAm (spectrum a), SBS-g-NIPAAm (spectrum b), and SBS (spectrum c).

reaction of the PNIPAAm homopolymer to SBS. However, beyond the concentration of 3×10^{-4} mol/20 mL of toluene, the percentage of grafting and grafting efficiency decreased. Because the recombination of primary radicals and the termina-

tion reaction of growing grafted chains can be enhanced at higher initiator concentrations, the increase of the initiator concentration usually results in a decrease of the grafting percentage. Table VII shows that the ratio of the conversion of grafting copolymerization to those of homopolymerization (C_g/C_h) increased and reached a maximum value of 0.23 when the initiator concentration was increased to 3×10^{-4} mol/20 mL of toluene, then it decreased with increasing concentration of the initiator.

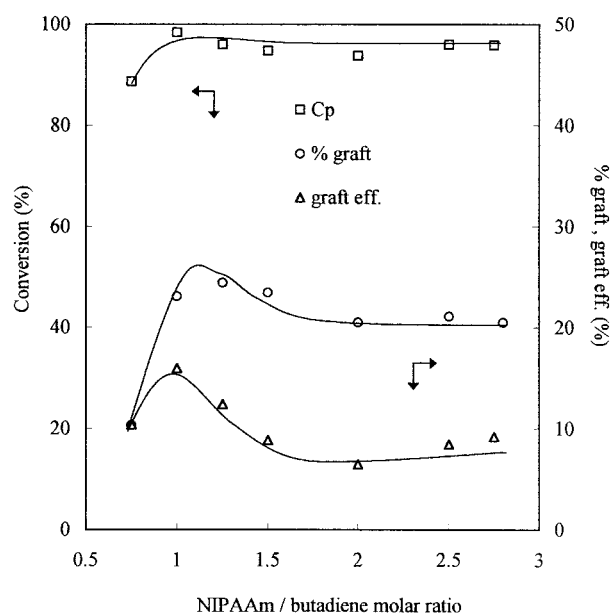


Figure 2 The effect of the NIPAAm/butadiene molar ratio in the grafting reaction on the NIPAAm conversion and grafting percentage.

Table IV NIPAAm Conversion of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Toluene

NIPAAm/Butadiene Molar Ratio	C_p (%)	C_g (%)	C_h (%)
0.75	88.7	11.1	77.6
1.0	98.4	18.7	79.7
1.25	96.0	13.8	82.2
1.5	94.8	9.8	85.0
2.0	93.8	6.6	87.2
2.5	96.0	8.3	87.7
3.0	95.9	8.8	87.1

The experimental conditions were 1 g of SBS, 1×10^{-4} mol BPO, and 20 mL of toluene with a reaction time of 4 h and a reaction temperature of 75°C.

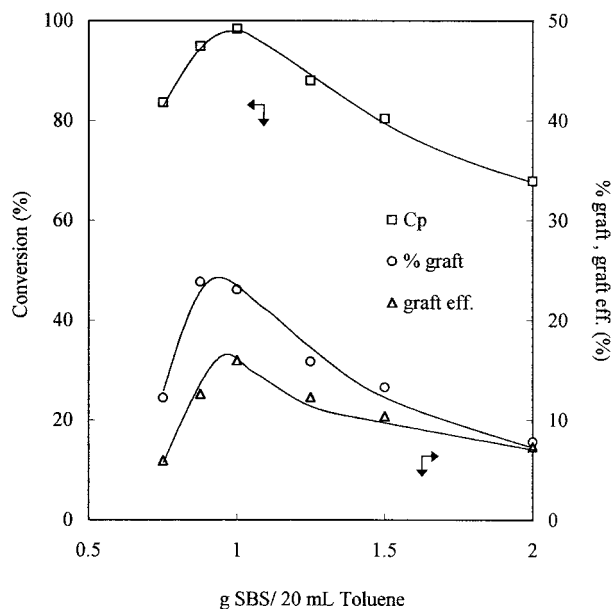


Figure 3 The effect of the SBS concentration in the grafting reaction on the NIPAAm conversion and grafting percentage.

Effect of Reaction Temperature on Grafting Percentage

The effect of a reaction temperature range of 65–90°C on the conversion, grafting efficiency, and grafting percentage is shown in Figure 6. It is clear that the grafting degree was gradually increased with the increase of the grafting temperature, but the grafting reaction did not happen when the reaction temperature was lower than 65°C. From 70 to 90°C the grafting percentage increased gradually. This result is also shown in Table VIII. The conversion of graft copolymeriza-

Table V NIPAAm Conversion of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Toluene

SBS Concentration (g/20 mL Toluene)	C_p (%)	C_g (%)	C_h (%)
0.75	83.6	5.0	78.6
0.875	94.9	13.6	81.3
1.0	98.4	18.7	79.7
1.25	88.0	10.8	77.2
1.5	80.4	8.5	71.9
2.0	67.9	4.9	63.0

The experimental conditions were 0.013 mol NIPAAm, 1×10^{-4} mol BPO, and 20 mL of toluene with a reaction time of 4 h and a reaction temperature of 75°C.

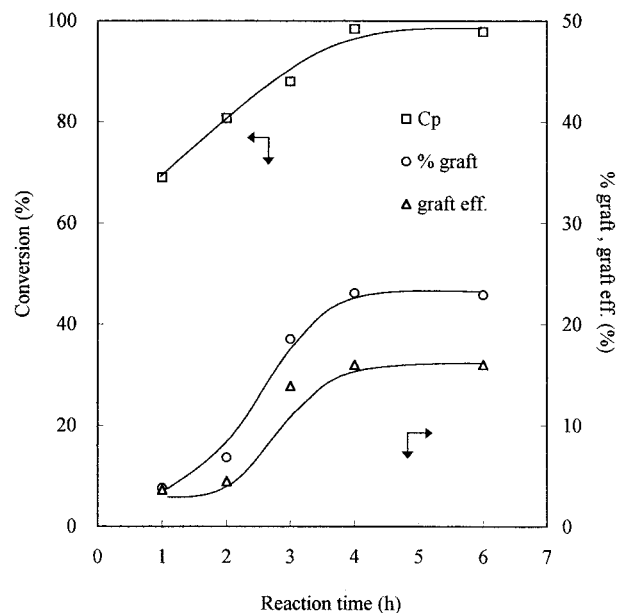


Figure 4 The effect of the reaction time in the grafting reaction on the NIPAAm conversion and grafting percentage.

tion was zero when the reaction temperature was 65°C and then increased gradually with the increase of temperature. It was similar to the result obtained from NIPAAm grafted onto polypropylene,⁵⁶ but it differed from the result obtained from NIPAAm grafted onto ethylene vinyl acetate.⁵⁷

Water Content of Grafted Copolymer Membranes

Because of the existence of a hydrophilic group (amido-, —CONH—) in NIPAAm, the water content of SBS is improved by graft copolymeriza-

Table VI NIPAAm Conversion of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Toluene

Reaction Time (h)	C_p (%)	C_g (%)	C_h (%)
1	69.0	2.5	66.5
2	80.7	3.6	77.1
3	88.0	12.2	75.8
4	98.4	18.7	79.7
6	97.2	18.5	78.7

The experimental conditions were 1 g of SBS, 0.013 mol NIPAAm, 1×10^{-4} mol BPO and 20 mL of toluene with a reaction temperature of 75°C.

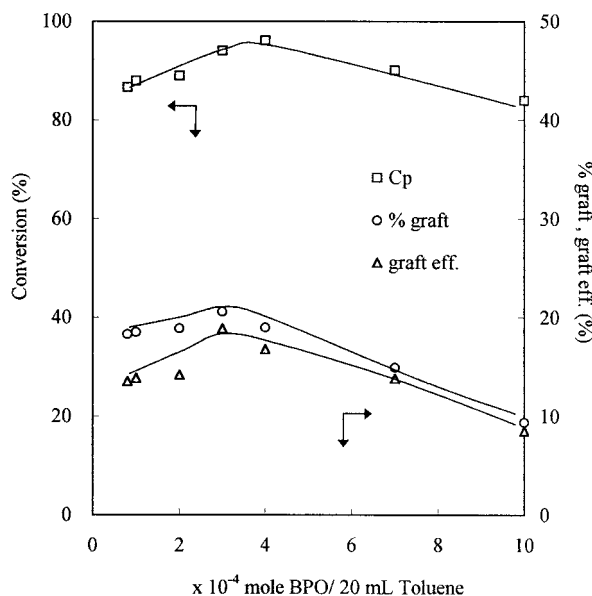


Figure 5 The effect of the initiator concentration in the grafting reaction on the NIPAAm conversion and grafting percentage.

tion. The improvement of water absorption for SBS is indicated by the water contents of copolymer membranes. Figure 7 shows the water absorbing kinetics of the grafted copolymer membranes with different grafting percentages at 25°C. The equilibrium water content of the copolymer membrane increased with the percentage of grafting. This result explicitly indicated that the hydrophilic group of NIPAAm affected the water

Table VII NIPAAm Conversion of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Toluene

Initiator Concentration ($\times 10^{-4}$ mol/20 mL Toluene)	C_p (%)	C_g (%)	C_h (%)	C_g/C_h
0.8	86.7	11.6	75.1	0.15
1.0	88.0	12.2	75.8	0.16
2.0	89.0	12.6	76.2	0.17
3.0	94.1	17.8	76.3	0.23
4.0	96.1	16.1	80.0	0.20
7.0	90.1	12.4	77.7	0.16
10.0	84.0	7.2	76.8	0.09

The experimental conditions were 1 g of SBS, 0.013 mol NIPAAm, and 20 mL of toluene with a reaction time of 4 h and a reaction temperature of 75°C.

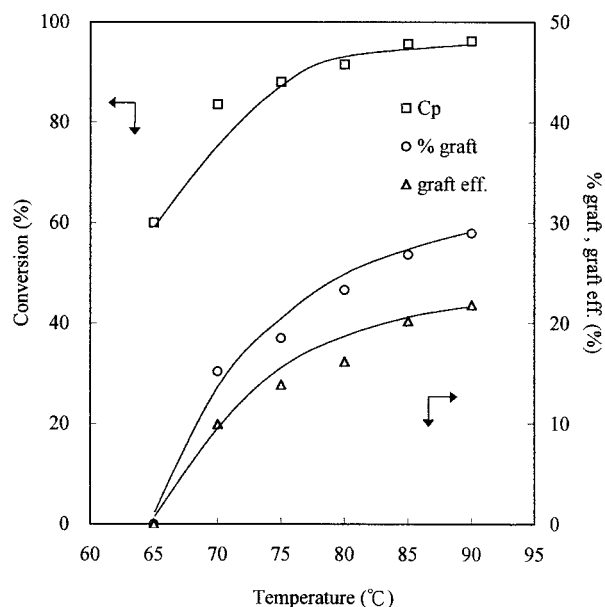


Figure 6 The effect of the reaction temperature in the grafting reaction on the NIPAAm conversion and grafting percentage.

absorbency of grafted membranes. When the degree of NIPAAm grafted onto SBS increased, the role of the hydrophilic PNIPAAm in SBS-g-NIPAAm became more important.

Temperature Sensitivity of Grafted Copolymer Membranes

Figure 8 shows the equilibrium water contents of the grafted membranes with different grafting percentages at different temperatures. The equilibrium water contents of the copolymer mem-

Table VIII NIPAAm Conversion of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Toluene

Reaction Temp. (°C)	C_p (%)	C_g (%)	C_h (%)
65	60.1	0	60.1
70	83.5	8.3	75.2
75	88.0	12.2	75.8
80	91.5	14.7	76.8
85	98.7	21.8	76.9
90	96.2	21.4	74.8

The experimental conditions were 0.013 mol NIPAAm, 1×10^{-4} mol BPO, and 20 mL of toluene with a reaction time of 4 h.

branes with various grafting percentages decreased rapidly between 30 and 35°C. As in previous reports,⁴⁷⁻⁵⁰ the NIPAAm contained a hydrophilic group (amido-, —CONH—) and a hydrophobic group (isopropyl-). The hydrophilic group in the polymer structure forms an intermolecular hydrogen bond with the surrounding water at low temperature (below the gel-transition temperature). Hence, water penetrating into the SBS-*g*-NIPAAm membrane was in a bound state at low temperature. The water molecule undergoes enthalpy during the increase of temperature, and the hydrophilic group in the NIPAAm is turned into an intramolecular hydrogen bond in this condition. At the same time, the hydrophobic force of the isopropyl group of NIPAAm increases. These two results made the water molecule inside the membrane change from a bound state to a free state, releasing it from the membrane. This phenomenon made the water contents of the grafted membranes rapidly decrease at the gel-transition temperature: the higher the degree of NIPAAm grafted onto SBS, the more significant the temperature sensitivity of the membrane.

CONCLUSIONS

The grafting of NIPAAm onto SBS by means of the chemical graft method was successfully per-

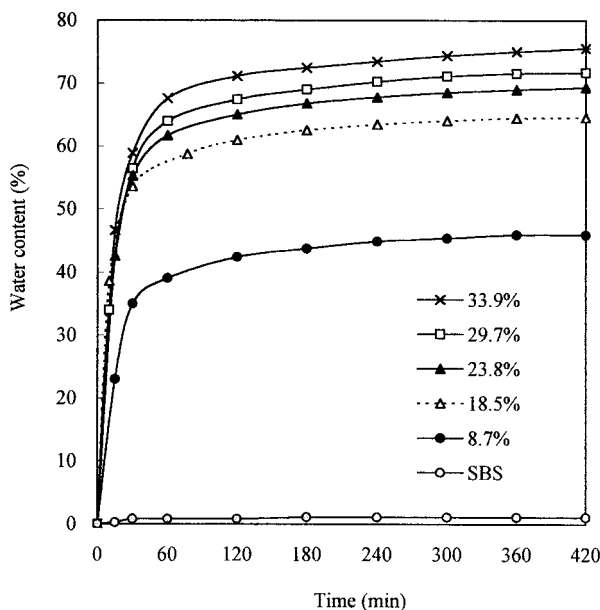


Figure 7 The water absorption of SBS-*g*-NIPAAm copolymer membranes with different amounts of grafting as a function of time at 25°C.

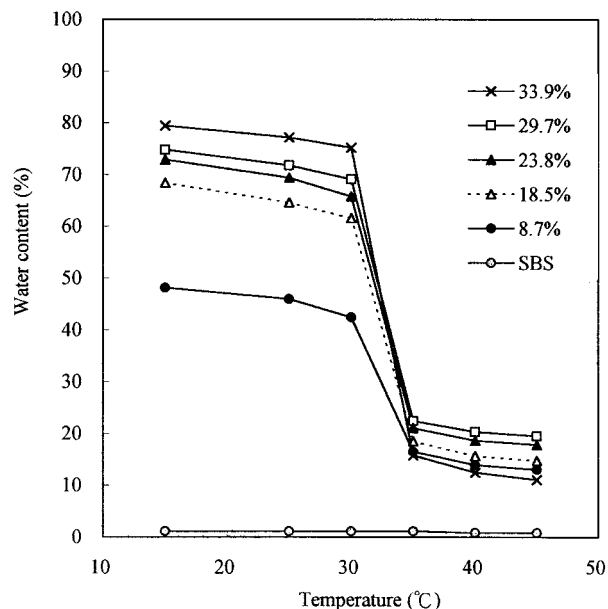


Figure 8 The equilibrium water content of the SBS-*g*-NIPAAm copolymer membrane with different amounts of grafting as a function of temperature.

formed. Under the reaction conditions chosen, the NIPAAm/butadiene molar ratio, SBS concentration, reaction time, initiator concentration, and reaction temperature were determined for optimal grafting.

The following conclusions were reached:

1. The grafting percentage of SBS-*g*-NIPAAm increased with the NIPAAm/butadiene molar ratio to a maximum value at 1.25.
2. The grafting percentage of SBS-*g*-NIPAAm increased with the concentration of SBS in 20 mL of toluene to a maximum value at 1 g, then it dramatically decreased with an increasing SBS amount in the reaction mixture.
3. The grafting percentage of SBS-*g*-NIPAAm increased gradually with the reaction time to a maximum value at 4 h.
4. The grafting percentage of SBS-*g*-NIPAAm had a maximum value at 3×10^{-4} mol of initiator (BPO) in 20 mL of toluene, then it decreased with the initiator concentration.
5. The grafting percentage of SBS-*g*-NIPAAm increased with the reaction temperature, but the grafting reaction did not happen when the reaction temperature was lower than 65°C.

Moreover, the membranes of SBS-*g*-NIPAAm with different grafting percentages possessed wa-

ter absorptivity and temperature sensitivity, which are particular properties of NIPAAm.

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REFERENCES

- Hoiden, G.; Bishop, E. T.; Legge, N. R. *J Polym Sci C* 1969, 26, 37.
- Ikada, Y. *Biomaterials* 1994, 15, 725.
- Uyama, Y.; Tadokoro, H.; Ikada, Y. *J Appl Polym Sci* 1990, 39, 489.
- Tomita, N.; Tamai, S.; Okajima, E.; Hirao, Y.; Ikeuchi, K.; Ikada, Y. *J Appl Biomater* 1994, 5, 175.
- Fujimoto, K.; Tadokoro, H.; Ueda, Y.; Ikada, Y. *Biomaterials* 1993, 14, 441.
- Fujimoto, K.; Inoue, H.; Ikada, Y. *J Biomed Mater Res* 1993, 27, 1559.
- Okada, T.; Ikada, Y. *J Biomed Mater Res* 1992, 26, 2569.
- Kulik, E. A.; Kato, K.; Ivanchenko, M. I.; Ikada, Y. *Biomaterials* 1993, 14, 763.
- Hsiue, G. H.; Yang, J. M.; Wu, R. L. *J Biomed Mater Res* 1988, 22, 405.
- Yang, J. M.; Hsiue, G. H. *Angew Makromol Chem* 1990, 179, 99.
- Yang, J. M.; Hsiue, G. H. *J Appl Polym Sci* 1990, 39, 1475.
- Yang, J. M.; Hsiue, G. H. *J Appl Polym Sci* 1990, 41, 1141.
- Yang, J. M.; Hsiue, G. H. *Angew Makromol Chem* 1995, 231, 1.
- Yang, J. M.; Hsiue, G. H. *J Biomed Mater Res* 1996, 31, 281.
- Hsiue, G. H.; Yang, J. M. *Makromol Chem* 1991, 192, 2687.
- Yang, J. M.; Wang, M. C.; Hsu, Y. G.; Chang, C. H.; Lo, S. K. *J Membr Sci* 1998, 138, 19.
- Uchida, E.; Uyama, Y.; Ikada, Y. *J Appl Polym Sci* 1993, 41, 677.
- Uchida, E.; Uyama, Y.; Ikada, Y. *J Appl Polym Sci* 1993, 47, 417.
- Yang, J. M.; Jong, Y. J.; Hsu, K. Y. *J Biomed Mater Res* 1997, 35, 175.
- Yang, J. M.; Wang, M. C.; Hsu, Y. G.; Chang, C. H. *J Membr Sci* 1997, 128, 133.
- Yang, J. M.; Wang, M. C.; Hsu, Y. G. *J Appl Polym Sci* 1997, 65, 109.
- Yang, J. M.; Jong, Y. J.; Hsu, Y. G.; Chang, C. H. *J Biomed Mater* 1998, 39, 86.
- Sacak, M.; Sertkaya, F.; Taul, M. *J Appl Polym Sci* 1992, 44, 1737.
- Sacak, M.; Pulat, E. *J Appl Polym Sci* 1989, 38, 539.
- Sanli, O.; Pulat, E. *J Appl Polym Sci* 1993, 47, 1.
- Sacak, M.; Pulat, E. *J Appl Polym Sci* 1989, 38, 539.
- Tsubokawa, N.; Ishida, H. *J Polym Sci Part A* 1992, 30, 2241.
- Tsubokawa, N.; Inagaki, M.; Endo, T. *J Polym Sci Part A* 1993, 31, 563.
- Pradhan, A. K.; Pati, N. C.; Nayak, P. L. *J Appl Polym Sci* 1982, 27, 1873.
- Schanberg, E.; Hoigne, J. *J Polym Sci* 1970, 8, 693.
- Yasuda, H. *Plasma Polymerization*; Academic: Tokyo, 1985.
- Wang, C. C.; Hsiue, G. H. *J Polym Sci Part A* 1993, 31, 1307.
- Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* 1986, 19, 1804.
- Cohn, D.; Tal-atias, I. *J Macromol Sci Chem* 1988, A25, 373.
- Kostov, G. K.; Atanassov, A. N. *J Appl Polym Sci* 1993, 47, 361.
- Heieh, Y.; Dugh, C. *J Appl Polym Sci* 1984, 29, 2547.
- Kostov, G. K.; Atanassov, A. N. *J Appl Polym Sci* 1993, 47, 361.
- Memetea, T.; Stannett, V. *Polymer* 1979, 20, 465.
- Ishigaki, I.; Sugo, T.; Senoo, K.; Okada, T.; Okamoto, J.; Machi, S. T. *J Appl Polym Sci* 1982, 27, 1033.
- Oneill, T. *J Polym Sci* 1972, 10, 569.
- Needles, H.; Alger, K. W. *J Appl Polym Sci* 1978, 22, 3405.
- Yang, J. M.; Chaian Chang, C. P.; Hsu, K. Y. *J Membr Sci* 1999, 153, 175.
- Fujimoyo, K.; Takebayashi, Y.; Inoue, H.; Ikada, Y. *J Polym Sci Polym Chem* 1993, 31, 1035.
- Tseng, Y. C.; Park, K. *J Biomed Mater Res* 1992, 26, 373.
- Kochwa, S.; Litwak, R. S. *Ann NY Acad Sci* 1977, 283, 37.
- Yuan, G.; Zhao, Y. *Polymer* 1997, 38, 119.
- Freltas, R. F. S.; Cussler, E. L. *Sep Sci Technol* 1987, 22, 911.
- Dong, L. C.; Hoffman, A. S. *J Controlled Release* 1986, 4, 223.
- Heskins, M.; Guillet, J. E. *J Macromol Sci Chem* 1968, A2, 1441.
- Hirotsu, S. *J Phys Soc Jpn* 1987, 56, 233.
- Saroop, U. K.; Sharma, K. K.; Saroop, M.; Jain, K. K.; Misra, A.; Maiti, S. N. *Eur Polym J* 1988, 24, 689.
- Lee, W. F.; Lai, C. C. *J Appl Polym Sci* 1994, 51, 2175.
- Lee, W. F.; Lai, C. C. *J Appl Polym Sci* 1995, 55, 1197.
- Lee, W. F.; Tu, Y. M. *J Appl Polym Sci* 1999, 74, 1234.
- Lee, H. S.; Lee, T. Y. *Polymer* 1997, 38, 4505.
- Minghong, W.; Bao, B.; Chen, J.; Xu, Y.; Zhou, S.; Ma, Z. T. *Radiat Phys Chem* 1999, 56, 341.
- Minghong, W.; Chen, J.; Zhogli, D.; Ma, Z. T. *Radiat Phys Chem* 1996, 48, 525.