

## Effects of Dyeing Temperature and Molecular Structure on the Dye Affinity of Polyurethane Films containing Polyethylene Glycol Segments

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### Abstract

The dyeing behavior of segmented polyurethane containing copolymerized polyethylene glycol soft segments was investigated. Four types of segmented polyurethane were prepared by controlling the aggregation of the hard segments and the mobility of polyethylene glycol in the soft segments. Dyeing rate curves and sorption isotherms were obtained for direct dyes at various temperatures along with the swelling ratios of the different segmented polyurethane samples. The sorption of CI Direct Red 28 by these samples is shown to decrease with increasing dyeing temperature, with the swelling ratio of the segmented polyurethane film also decreasing. Changes in the tensile strength of the films before and after dyeing with CI Direct Red 28 are shown to be related to the degree of aggregation of the hard segments, as well as to the amount of dye used.

**Keywords:** Direct dye; Aggregate structure; Polyurethane; Dye affinity; Polyethylene glycol

### Introduction

The high flexibility of polyurethane resin, even at low temperatures, and the fact that its molecular structure can be modified to produce fibers or films makes it an ideal material for cloth and interior linings. Segmented polyurethane (SPU) is commonly used as a raw material in the production of polyurethane elastic fibers as well as artificial and synthetic leather, but its hydrophobic nature means that disperse dyes are generally used despite their color fastness and colorability being unsatisfactory. The ability to dye SPU with water-soluble dyes is particularly important for artificial and synthetic leather, particularly in the single-bath dyeing of artificial leather (nonwoven nylon fibers impregnated with polyurethane resin) or dyeing of synthetic leather fashion garments. In industry, SPU has been rendered responsive to acid dyes by synthesizing soft segments through copolymerization with polyethylene glycol (PEG) [1,2] or by introducing dyeing sites [3,4] through copolymerization with tertiary amino groups or tertiary nitrogen chain extenders.

In a previous study [5] SPU films with soft segments prepared using different relative contents of PEG and polytetramethylene glycol (PTMG) were investigated in relation to their affinity to acid dyes. The tensile strength of these films was found to decrease with increasing PEG concentration, whereas the elongation to breaking tended to increase. The affinity of the SPU films for acid leveling-type dyes was low, but the films with higher PEG contents were readily stained with milling-type dyes. Elsewhere [6] dyeing rates and sorption isotherms for direct and milling-type acid dyes were obtained for SPU films with various PEG to PTMG composition ratios. From this, a dyeing mechanism was proposed involving interactions between the dye and hydrophilic PEG groups in SPU soft segments [6] in which dyeing is presumed to occur through van der Waals forces that exist between the dye and hydrophobic urethane moieties.

Based on this knowledge, the present study was conducted by first investigating the effect of dyeing temperature on the interaction between a dye and the hydrophilic PEG groups in the soft segments. For this, a SPU sample was prepared using only PEG for the soft segments in order to maximize its affinity for direct dyes. Since the aggregation of hard segments in SPU restricts the movement of PEG chains, the

impact of this on dyeing was also investigated. Finally, SPU samples were prepared using different combinations of PEG and PTMG for the soft segments, and their tensile strengths and breaking elongations were compared. The measured dye uptake for each SPU and swelling ratios of the SPU films in water makes it possible to optimize the dyeing conditions for acid and direct dyes used in industry, meaning that this study should greatly contribute to improving the industrial dyeing of elastic fibers and artificial/synthetic leather.

### Experimental Methods

#### Chemicals and reagents

The PTMG and ethylene glycol used in this study were procured from Mitsubishi Chemical Corp.; dimethylformamide (DMF) was obtained from Mitsubishi Gas Chemical Company, Inc.; PEG was purchased from NOF Corp. and MDI was procured from Tosho Corp. The 1,4-butanediol (1,4BD), 1,6-hexanediol (1,6HG) and CI Direct Red 28 were purchased from BASF Corp., UBE Industries, Ltd. and Wako Pure Chemical Industries, Ltd., respectively.

#### Preparation of the SPU solution

A total of five SPU solutions were prepared as follows: Solution 1 was prepared using only PEG for the soft segments; Solutions 2, 3 and 5 were prepared with a PEG to PTMG weight ratio of exactly 80:20, while for Solution 4 a weight ratio of 78:22 was used. As shown in Table 1, SPU was synthesized in each instance by extending the chain after pre-polymerization, with all reactions being performed in DMF under a nitrogen flow. The solid matter content and viscosity of all the SPU

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Solution	1		2		3		4		5	
Prepolymer reaction* (soft segments)	PEG2000	0.50	PEG2000	0.40	PEG2000	0.40	PEG600	1.20	PEG2000	0.40
	MDI	1.00	PTMG2000	0.10	MDI	0.30	MDI	0.80	PTMG2000	0.10
Chain extension* (hard segments)	1,4BD	1.50	1,4BD	1.50	1,4BD	1.50	1,4BD	1.50	ethylene glycol	0.75
	MDI	1.00	MDI	1.00	MDI	1.30	MDI	1.00	1,6HD	0.75
PEG/PTMG (wt%)	100/0		80/20		80/20		78/22		80/20	
NCO (%)	10.28		10.28		10.28		13.40		10.28	

PEG: polyethylene glycol; PTMG: polytetramethylene glycol; MDI: 4,4'-diphenylmethanediisocyanate; 1,4BD: 1,4-butanediol; 1,6HG: 1,6-hexanediol  
\*all values in mol.

**Table 1:** Soft- and hard-segment contents and reaction methods used to prepare the five segmented polyurethanes investigated here.

solutions were adjusted to 30 wt% and 50 Pa-s (at 30°C), respectively. Figure 1 shows the chemical structure of the PTMG- and PEG-based soft segments, as well as that of the 1,4BD-based hard segments.

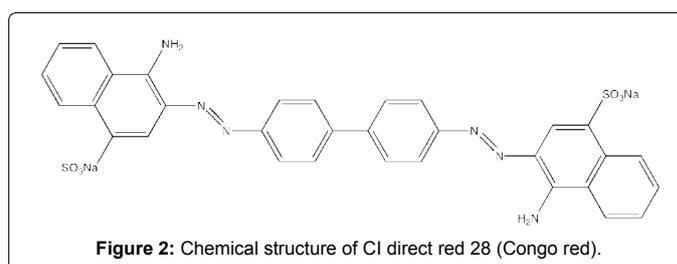
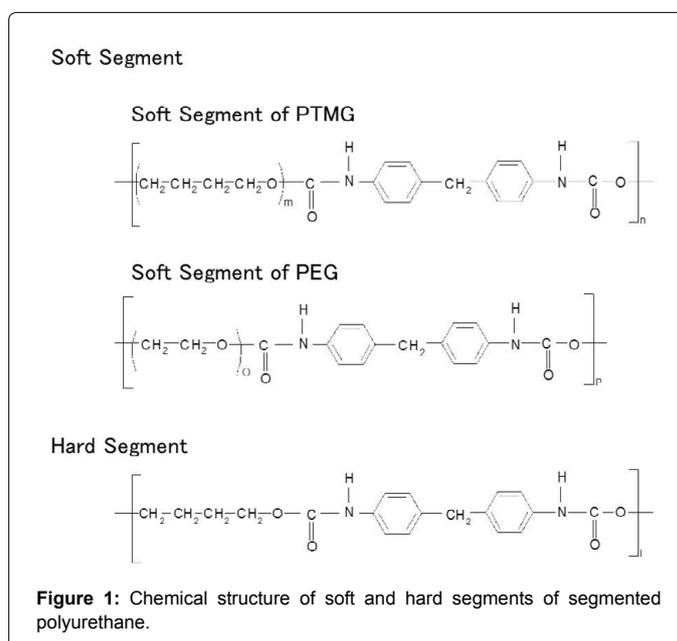
### Preparation of cast films

The five pre-prepared SPU solutions were individually flow cast onto release paper using a Baker-type applicator (Tester Sangyo Co., Ltd.) to form solution layers of a specific thickness. These layers were then placed in a dryer for 20 minutes at 120°C to obtain cast films. Using this method, films of two different thicknesses (50 and 60 μm) were obtained.

### Measurement of dyeing rate curves and sorption isotherms

As all of the cast films were found to swell in water, they were immersed in boiling water for 10 minutes before dyeing with the direct dye CI Direct Red 28, the chemical structure of which is shown in Figure 2. The dyeing rates for the films cast from Solution 1 were measured at dyeing temperatures of 30°C, 50°C, 70°C and 90°C by immersing for 120 minutes in a dye bath prepared with a material-to-liquor ratio of 1:200, and dye and sodium chloride concentrations of 0.1 and 1 g/L, respectively. Films 2-5 were dyed at 90°C for 80 minutes. All dyed films were washed twice for 1 minute in room-temperature water at a material-to-liquor ratio of 1:2000, after which the samples were washed with water and dried in preparation for dye affinity tests. The dye content of each cast film was obtained by dissolving each film in room temperature DMF solution and, using a calibration curve prepared in advance from DMF solutions of the dyes, deducing the dye concentration from the absorbance of the solution. The dye concentration in each film was then calculated based on its absolute dry mass, as measured with an infrared electronic moisture meter (AD-4715, A&D Co. Ltd.) [6].

Sorption isotherms for the films cast from Solution 1 were measured at 30°C, 50°C, 70°C and 90°C using a dyeing time of 120 minutes; i.e., the sorption equilibration time determined from the dyeing rate curves. For the films cast using Solution 2-5, the dye temperature was set to 90°C and the samples were immersed for 80 minutes in the same dye liquor described above. The samples were left to swell and were washed using the same procedure as for the measurement of the dyeing rates. The sorption isotherms were derived from the sorbed dye concentration,  $[D]_p$  and the dye concentration in the bath after dyeing,  $[D]_s$ ; the former was determined by colorimetry after dissolving the films in DMF, while the latter was deduced from the initial concentration in the bath and  $[D]_p$ . The thermodynamic parameters were calculated by applying the standard method for cellulose fiber systems interacting with direct dyes [7]. The effective volumes of the samples were calculated from the measured area swelling ratios of the



cast films, as described in the following section. The films had an initial thickness of 60 μm and water-swelling was assumed to occur uniformly in all directions.

### Measurement of water-swelling ratio

Water-swelling measurements performed by first cutting each 60-μm-thick cast film into square 50 × 50 mm specimens. For Solution 1, the specimens were immersed in tanks of deionized water held at different temperatures and photographed using a digital camera (Optio 750Z, Pentax). For Solution 2-5, the specimens were similarly photographed after immersion for 10 minutes in glass petri dishes filled with deionized water at 20°C. Image analysis software (Image-Pro Plus v. 6.3, Media Cybernetics) was used to measure the film area in each

image, and this was then compared with the area of the dry films to determine the water-swelling ratio at different temperatures.

### Measurement of tensile strength, breaking elongation and thermal softening

The tensile strength and breaking elongation of the 60- $\mu\text{m}$  thick cast films were measured before and after dyeing with CI Direct Red 28. Reference films were also prepared under the same temperature and wetting conditions, but were immersed in dye-free water. Test specimens were prepared from the cast films using a type 2 cutting die, as stipulated in the JISK7113 standard. In light of the sensitivity of the specimens to temperature and humidity, they were held at 20°C and 50 % relative humidity for more than 24 hours prior to carrying out the tensile tests. These tests were performed using an Instron Model 5569 testing system (Instron Japan Co., Ltd.) operated at 400 mm/minute with a chuck spacing of 60 mm. Measurements were not performed for samples prepared from Solution 1 and 2, as the strength and ductility of these were already known from a previous study [5].

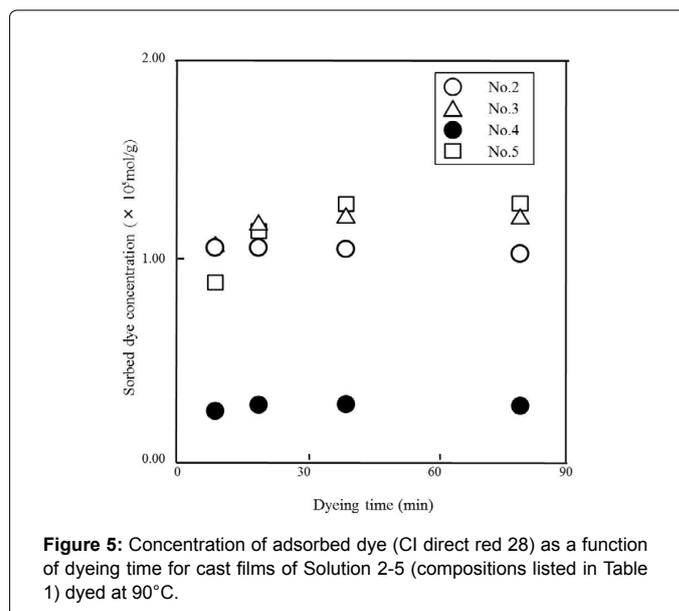
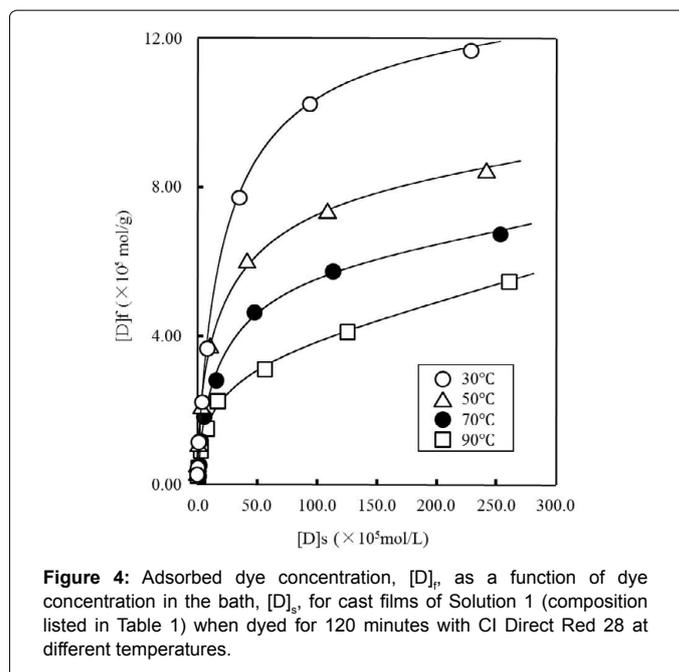
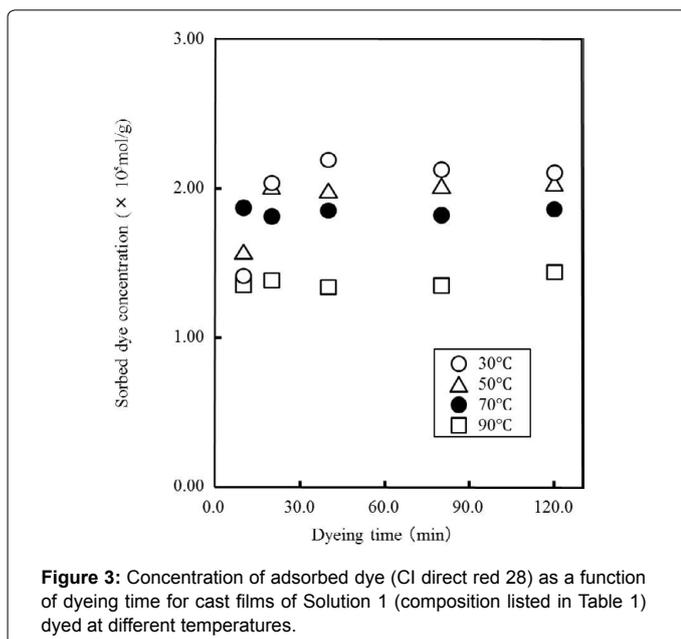
Thermal softening experiments were performed with a TMA-50 thermo-mechanical analyzer (Shimadzu Corp.) on 50- $\mu\text{m}$ -thick cast films prepared from Solutions 2-5 using the needle insertion method. Measurements were taken under a nitrogen atmosphere and 0.05 N load, with the temperature being increased from 25°C to 250°C at 10°C/minute.

## Results and Discussion

### Affinity of the cast films for direct dye

**Dyeing rate curves:** Figure 3 shows the sorption curves for films produced from Solution 1 when dyed with CI Direct Red 28 at different temperatures. Note that the dyeing rate increases with temperature, with an apparent equilibrium being reached at 40, 20, and 10 minutes at 30°C, 50°C, 70°C and 90°C, respectively. The equilibrium concentrations of adsorbed dye are, however, higher at lower temperatures.

**Sorption isotherms:** Figure 4 shows the sorption isotherms obtained for cast films of Solution 1 at different temperatures. As



reported previously [6], the saturation concentration is not reached at any of these dyeing temperatures (from 30°C to 90°C). The dye concentrations in the films are higher at lower temperatures, with the separation between the isotherms increasing with  $[D]_s$ .

### Effect of cast film structure on dye affinity

**Dyeing rate curves:** Figure 5 shows the dyeing rate curves derived from the sorbed dye concentration (CI Direct Red 28) measured for cast films of Solution 2-5. The apparent equilibrium sorbed dye concentration is reached after about 40 minutes for each film, and is higher for those samples produced from Solution 5 than from Solution 3, 2 and 4 (in that order). This suggests that the presence of higher-order structures in the polymer reduces the dyeing rate.

**Sorption isotherms:** Figure 6 shows the sorption isotherms for cast films of Solution 2-5 when dyed with CI Direct Red 28. No saturation is observed in the case of Solution 1 and all sorbed dye concentrations are low, particularly with Solution 4. The dye concentrations for Solution 5 are slightly higher than those for Solution 3 and 2, in that order.

**Thermodynamic parameters:** The thermodynamic parameters calculated for the five cast films dyed with CI Direct Red 28 are listed in Tables 2 and 3. We see from this that films prepared from Solution 1, 2, 3 and 5 share a similar affinity for CI Direct Red 28, but that of Solution 4 is much lower. In terms of the structure of SPU in each film, the degree of hard-segment aggregation is the lowest with Solution 5, the mobility of hydrophilic soft segments containing PEG is increased with Solution 3, while Solution 2 produces a film with a standard composition.

### Water-swelling ratio of the cast films

Figure 7 shows that the swelling rate of 60- $\mu\text{m}$ -thick films cast from Solution 1 decreases as the temperature of the water increases. This behavior is similar to that of non-ionic surface-active agents with PEG hydrophilic groups exhibiting a clouding point, which suggests that more coordinated water molecules discharge from the soft segments of the SPU (composed of PEG and MDI) when the temperature is increased.

Figure 8 shows the measured water swelling rates for cast films of Solution 2-5, in which it can be seen that the degree of hard-segment aggregation and PEG mobility in the soft segments differ. The films are

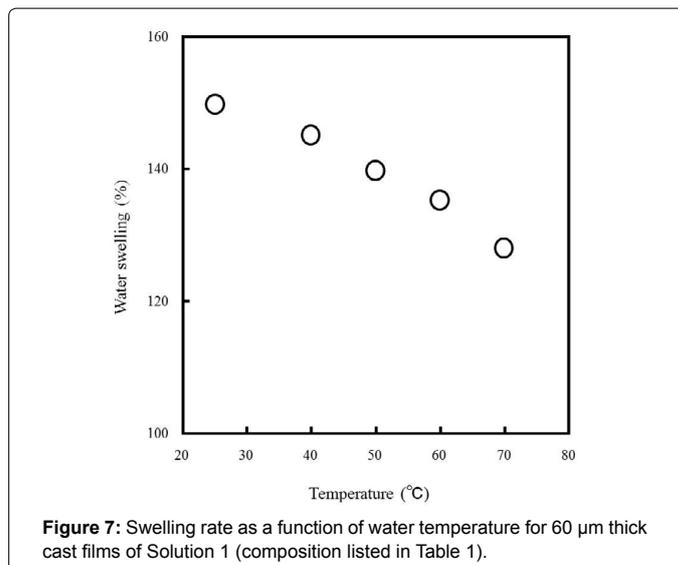


Figure 7: Swelling rate as a function of water temperature for 60  $\mu\text{m}$  thick cast films of Solution 1 (composition listed in Table 1).

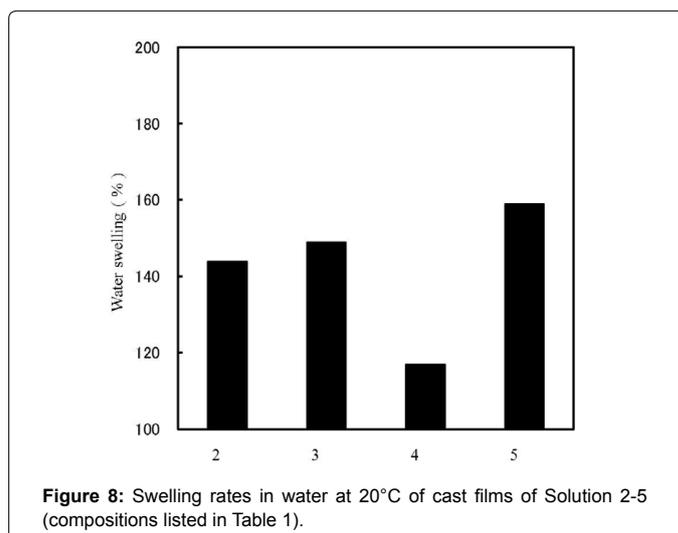


Figure 8: Swelling rates in water at 20°C of cast films of Solution 2-5 (compositions listed in Table 1).

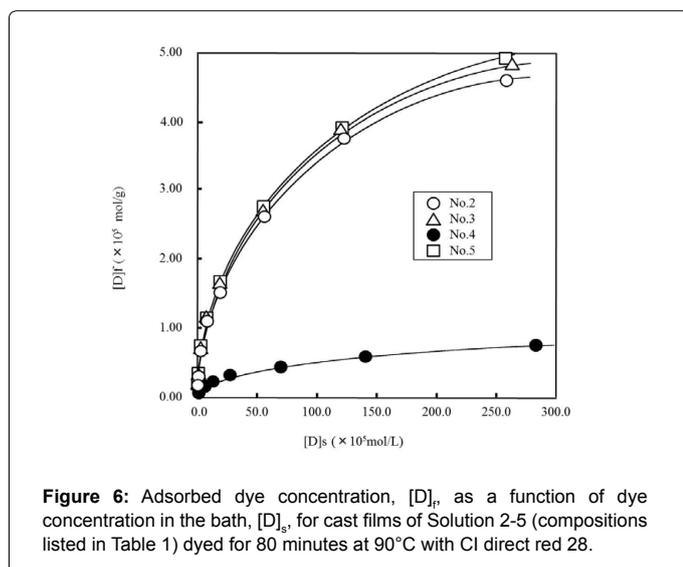


Figure 6: Adsorbed dye concentration,  $[D]_a$ , as a function of dye concentration in the bath,  $[D]_b$ , for cast films of Solution 2-5 (compositions listed in Table 1) dyed for 80 minutes at 90°C with CI direct red 28.

Film	$-\Delta\mu^\circ$ (kJ/mol)				$-\Delta H^\circ$ (kJ/mol)	$-\Delta S^\circ$ (J/K)
	30°C	50°C	70°C	90°C		
1	11	10	9	8	24	43

Table 2: Thermodynamic parameters calculated for dyeing films of Solution 1 (composition listed in Table 1) with CI Direct Red 28.

Solution	$-\Delta\mu^\circ$ at 90°C (kJ/mol)
2	8
3	8
4	2
5	8

Table 3: Standard affinities of CI Direct Red 28 for segmented polyurethane films.

ordered  $5 > 3 > 2 > 4$  in terms of their swelling rates in water, which suggests that the concentration of higher-order structures (which varies with the design of the polymer) influences its swelling properties in water.

### Tensile strength, breaking elongation and thermal softening

The tensile strength and breaking elongation for cast films of Solution 2-5 before dyeing are shown in Figures 9 and 10, respectively. Similar stress-strain curves were obtained for films produced from solution 2 and 3, and these have the same composition but differ in terms of the reaction method used for their soft segments, this may be due to their identical MDI contents. In the film produced from Solution 4, the soft segments (PEG oligomers with a molecular weight of 2300) contain polyurethane bonds arising from the reaction between PEG (molecular weight = 600) and MDI. Since this film has a higher content of MDI, it therefore has a higher tensile strength than the other films but a lower breaking elongation. With Solution 5, the lower tensile strength and higher breaking elongation of the film suggests a low level of aggregation, which may stem from the random combination

of single-chain glycol and methylene groups of varying lengths in the hard segments.

The tensile strengths of the films decreases after dyeing, more so for Solution 2 and 3 than for 4 and 5 (Figure 9), but the change in their breaking elongation is not significant (Figure 10). This presumably reflects the effect of CI Direct Red 28 on the hard-segment aggregates in the films, in that the dye can generally penetrate both the interior of the soft segment and the surface of the hard segment. In other words, the films produced from Solution 2 and 3 were affected by dye molecules on their hard segment surface, resulting in a decrease in tensile strength. The composition of the Solution 5 film moderates aggregation, resulting in a low tensile strength that is only slightly reduced by dyeing. The similarly small decrease observed with the Solution 4 film is, on the other hand, the result of a low dye uptake, which is hindered by the restricted mobility of the PEG-containing hydrophilic soft segments in this sample. It is also believed that the difference in dye concentration between each film has a significant effect on their tensile strength. For

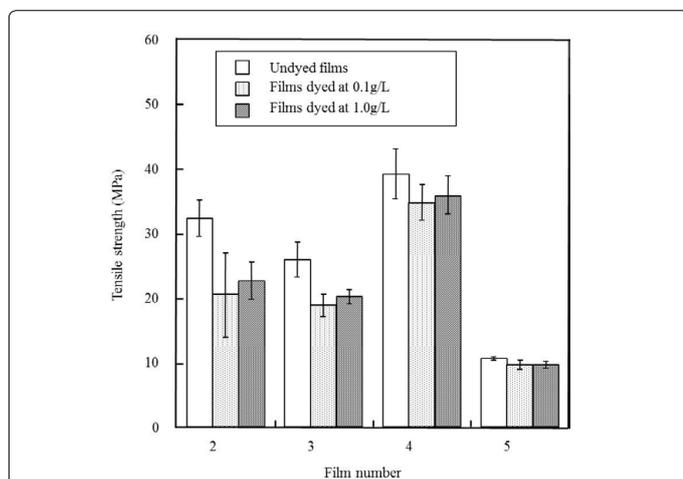


Figure 9: Comparison of the tensile strength of cast films of Solution 2-5 before and after dyeing. Error bars represent the standard deviation associated with each measurement.

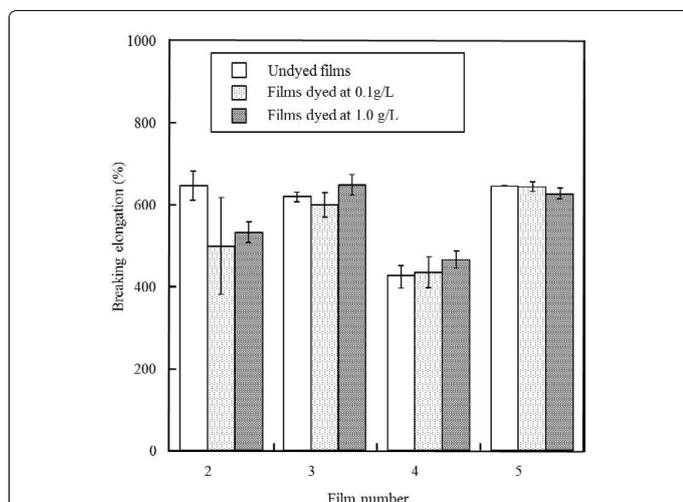


Figure 10: Comparison of the breaking elongation of cast films of Solution 2-5 before and after dyeing. Error bars represent the standard deviation of each measurement.

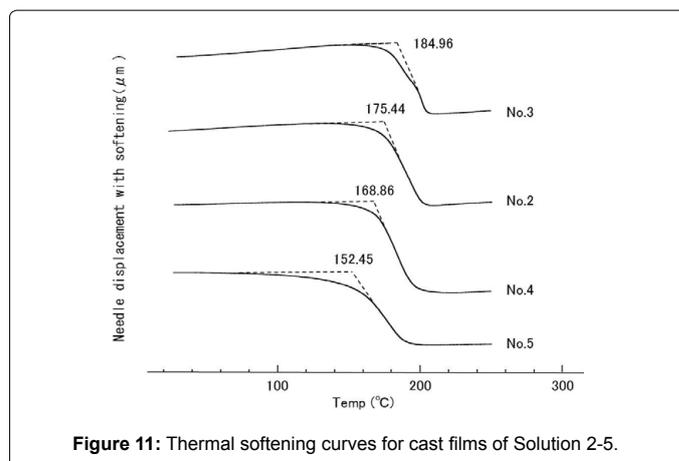


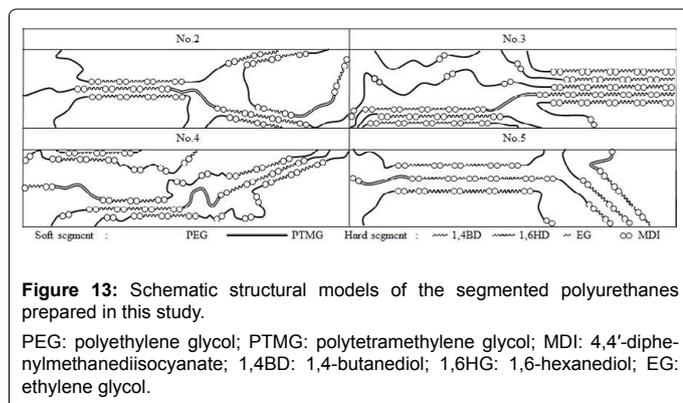
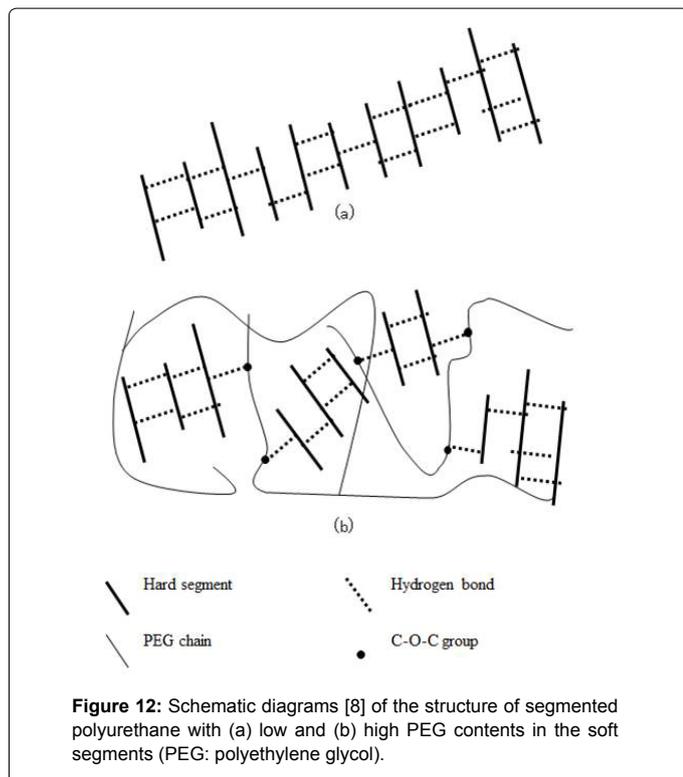
Figure 11: Thermal softening curves for cast films of Solution 2-5.

example, the Solution 2 film has lower tensile strength after dyeing than that of a film that is not dyed, which is likely due to the influence of the dye molecules on the hard segment surface. The higher tensile strength when a concentration of 1.0 g/L is used rather than 0.1 g/L could be due to dye molecules penetrating the soft segment. Since a greater quantity of dye has a more pronounced influence on the film due to an increased interaction with dye molecules, variation in the tensile strength is to be expected. Thus, undyed films had the highest tensile strength, followed by cast films dyed with 1 g/L and 0.1g/L of dye.

The thermal softening curves obtained for the different SPU films in Figure 11 show a clear difference in the softening behaviors of films produced from Solution 2 and 3, which contrasts with the similarity in their stress-strain properties (Figures 9 and 10). The higher softening temperature recorded for the Solution 3 film suggests that block copolymerization may have occurred and progressed to a higher order in this SssPU, resulting in greater hard segment aggregation than with Solution 2. Similarly, the lower softening temperature of the Solution 4 and 5 films reflects the lower aggregation propensity of their hard segments. In the case of Solution 4, this can be attributed to the urethane bonds in the soft segments, whereas with Solution 5 it is due to the random combination of single-chain glycol and methylene groups of varying lengths in the hard segments.

Previous studies of SPUs with the same compositions as those investigated here found that the number of hydrogen bonds in the hard segments decreases as the proportion of PEG in the soft segments increases, which is due to a reduction in crystallinity and a restriction of the molecular chains [8,9]. This difference in hydrogen bonding was confirmed by infrared spectroscopy based on the relative intensities of the absorption bands arising from urethane and hydrogen-binding urethane groups [8,9]. Figure 12 shows schematic diagrams based on this model of SPU aggregates with low and high PEG contents in the soft segments.

The different tensile strengths, breaking elongations, and thermal softening behaviors of the SPU samples may be interpreted as follows. Based on the results of the aforementioned study [8], the similar PEG contents in the soft segments of films produced from Solution 2-5 means that the moderation of hard-segment aggregation should also be similar. Nevertheless, the different physical properties of these samples presumably reflect different extents of hard-segment aggregation. The structural models proposed for these samples are shown in Figure 13.



## Conclusion

The dyeing rates and sorption isotherms of SPU films prepared by copolymerization of PEG in the soft segments and dyed with CI Direct Red 28 indicate on one hand a correlation between the extent of hard segment aggregation, and on the other a connection between the amount of adsorbed dye and the swelling rate in water. Coordinated water molecules tend to discharge from the SPU soft segments composed of PEG and MDI, with this increasing at higher dyeing temperatures. The different dyeing behaviors of the four types of SPU prepared with different higher-order structures confirm that dye uptake is also governed by how restricted the movement of the PEG chains is, which has been controlled here through the composition of the samples and the reaction methods used.

The tensile strength and breaking elongation of the films with high dye uptakes and low-level hard-segment aggregation, as well as those with low dye uptakes and restricted soft-segment mobility, vary little

after dyeing. In contrast, the tensile strength of the film with a high dye uptake and highly aggregated hard segments decreases significantly as a result of dyeing. This indicates that CI Direct Red 28 affects the degree of aggregation of SPU hard segments. The thermodynamic parameters of these SPUs also reveal that their affinity for CI Direct Red 28 depends on the level of aggregation of the hard segments, as well as on the mobility of the PEG-containing hydrophilic soft segments.

In conclusion, this study demonstrates a correlation between the dye (CI Direct Red 28) uptake, water-swelling ratio, and degree of hard-segment aggregation of different SPU compositions. These results should prove valuable from an industrial perspective, as the strength of dyed products is a clear marker of their quality. As color fastness is also crucial, this will be investigated in a future study into these SPUs.

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## Conflicts of Interest

The authors have no conflicts of interest to declare.

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