

Synthesis of Anionic Water-Borne Polyurethane with the Covalent Bond of a Reactive Dye

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ABSTRACT: We successfully synthesized an anionic water-borne polyurethane (PU) capable of reacting with a reactive dye to form a covalent bond with the dye molecule. The anionic water-borne PU was synthesized and grafted with the reactive dye to form a dyed PU. First, the PU prepolymer was synthesized from 4,4'-methylene bis(isocyanatocyclohexane), poly(tetramethylene glycol), 2,2'-bis(hydroxymethyl) propionic acid (as an anionic center), and triethyleneamide (as a neutralizer). Then, pure water was added to emulsify and disperse the prepolymer to form an anionic water-borne PU prepolymer. Finally, the extender *N*-(2-hydroxyethyl) ethylene diamine was used to extend the anionic water-borne prepolymer to form a PU polymer with hydroxyl groups that could further react with the reactive dye molecule. With respect to the heating properties, the dyed PU polymers exhibited higher glass-transition temperatures of the hard segment than those without dye molecules. However, neither the glass-transition temperature of the soft segment nor the melting temperature of the soft segment varied in the presence of dye molecules, but they were changed with various chain lengths of the soft segment. As for the mechanical properties, the modulus and strength of the dyed PU polymers decreased because of the bulkiness of their dye molecules, but the breaking elongation increased. Moreover, the inherent viscosity decreased in the presence of the dye molecules. As for the dyeing properties, the percentage of dye grafting was greater than 90%. The dye-grafted PU exhibited a lower percentage of migration than PU extended with ethylene diamine (without hydroxy groups) and also showed a higher grade of colorfastness to light. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 797–805, 2002; DOI 10.1002/app.10336

Key words: water-borne polyurethanes; reactive dyes; covalent bond of a dye molecule; colorfastness to light

INTRODUCTION

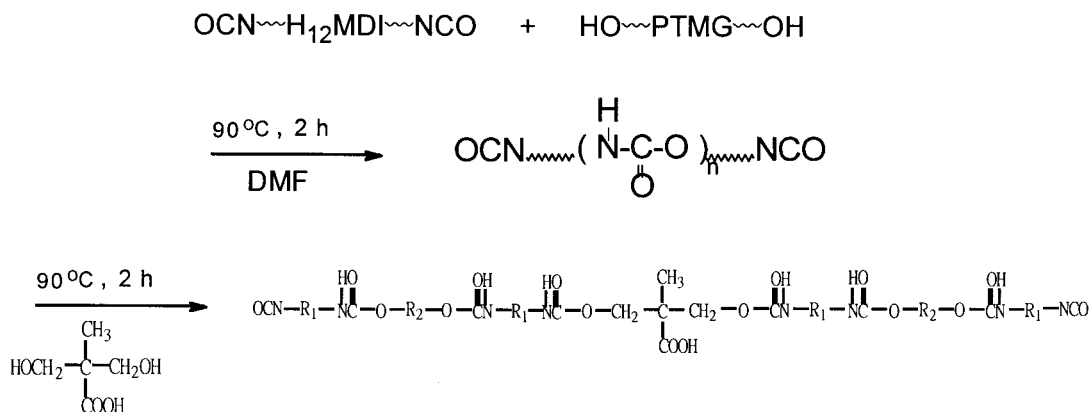
Polyurethane (PU) is a thermoplastic rubber with repeating hard and soft segments; therefore, it possesses good mechanical properties, such as

medium tensile strength and high elongation. It is used widely in synthetic leathers, fibers, and adhesives.^{1–8} Colored PU leather is mostly made of nonwoven fabrics coated with a mixture of pigment and PU resin. The color is dull, lacking brightness, and the leather has poor rubbing resistance. In addition, elastic PU fibers are usually dyed with an acid dye or a disperse dye at a high temperature of 90–100°C and a long time of 50–60 min.^{9–12} This wastes energy and time. In this study, we attempted to synthesize an anionic water-borne PU capable of reacting with a reac-

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Scheme 1 Synthesis of the PU prepolymer with NCO-terminated groups.

tive dye to form a covalent bond with the dye molecule. The anionic water-borne PU was synthesized and grafted with the reactive dye to form a dyed PU. The mechanical, thermal, and dye migration properties of the dye-grafted PU were studied.

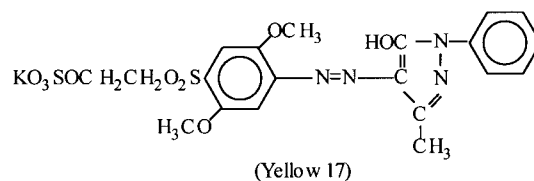
EXPERIMENTAL

Materials

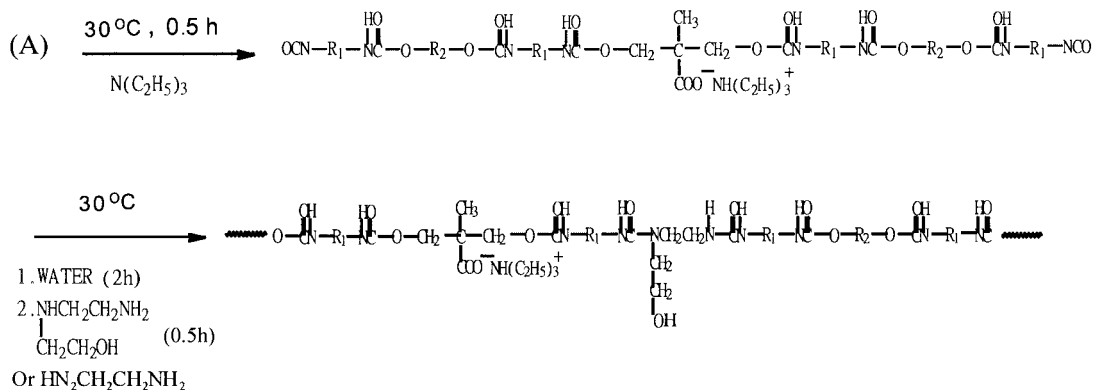
Poly(tetramethylene glycol) (PTMG) with molecular weights of 2000 and 1000 (Hodotani Co., Tokyo, Japan), 4,4'-methylene bis(isocyanatocyclohexane) (H_{12} -MDI), ethylene diamine (EDA), *N*-(2-hydroxyethyl) ethylene diamine (HEDA), triethyleneamide, 2,2'-bis(hydroxymethyl) propionic acid (DMPA), and *N,N'*-dimethylformamide (DMF) were used without further purification.

Three reactive dyes (Hochst, Frankfurt, Germany) with sulfuric acid esters of the β -hydroxyethyl sulfone series (CI Reactive Yellow 17, CI Reactive Red 4, and CI Reactive Blue 19) were used for reactions with the modified PU resin and were also used without further purification. The chemical structures of these three reactive dyes with sulfuric acid esters of β -hydroxyethyl sulfones were as follows:

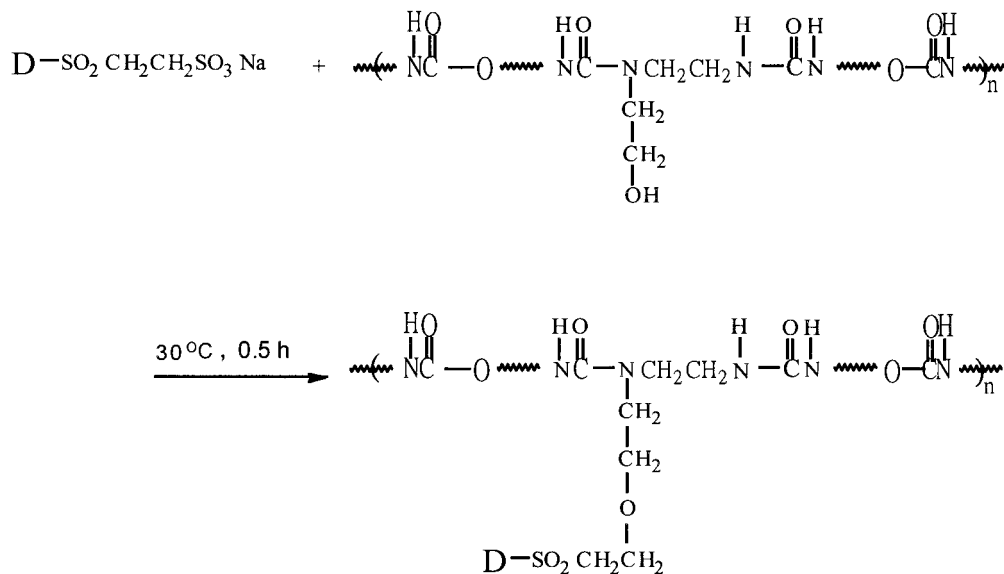
1. Y (yellow dye): CI Reactive Yellow 17



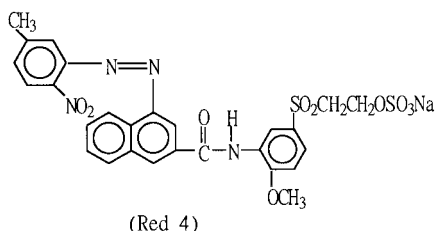
2. R (red dye): CI Reactive Red 4



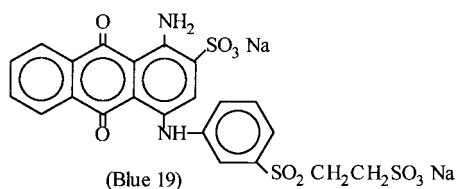
Scheme 2 Emulsification and chain extension of the PU prepolymer with hydroxyl side groups.



Scheme 3 Dye-grafted PU.



3. B (blue dye): CI Reactive Blue 19



Synthesis of Anionic Water-Borne PU with Hydroxy Side Groups

H_{12} -MDI was dissolved in DMF and poured into a reaction flask; the temperature was raised to 65°C under dry nitrogen. PTMG was also dissolved in DMF and added to the flask dropwise. The temperature was raised to 90°C for 2 h of reaction. The temperature was cooled to 30°C , DMPA was dissolved in DMF and added to the flask dropwise, and the temperature was increased to 90°C for 0.5 h. After the temperature was decreased to 30°C again, $N(\text{C}_2\text{H}_5)_3$ was added and stirred for 30 min, pure water was introduced and stirred for 2 h, and the extender HEDA (or EDA) in DMF was added at 30°C for 30 min. An

anionic water-borne (undyed) PU with hydroxyl groups was, therefore, synthesized (but PU was extended with EDA containing no hydroxyl groups). The reaction is shown in Schemes 1 and 2. The 3:1:1:1 H_{12} -MDI/PTMG/DMPA/chain extender (HEDA or EDA) ratio was labeled type A, and the 4:2:1:1 ratio was labeled type B.

Grafting of the Dye Molecule with the Anionically Modified PU

The reactive dye was first added to the PU solution in a reaction flask, and the temperature was raised to 30°C for 0.5 h under a slightly alkaline condition. The final solution was cast into films and washed with methanol to remove the unreacted dye in the film, as shown in Scheme 3.

Measurements

IR spectra of dyed and undyed PUs were obtained with a Hitachi model 260-50 type over a range of

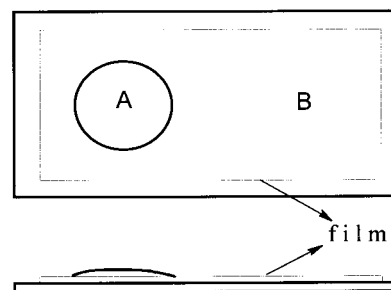


Figure 1 Glass plate for measuring the dye migration.

Table I Code of All PU Polymer Films

Code ^a	Component	Molar Ratio	Hard-Segment Content ^b (wt %)	Soft-Segment Content ^c (wt %)
1A	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA	3:1:1:1	50.59	49.41
1A-RB	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA/Dye-1	3:1:1:1:0.2	50.59	49.41
1A-RR	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA/Dye-2	3:1:1:1:0.2	50.59	49.41
1A-RY	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA/Dye-3	3:1:1:1:0.2	50.59	49.41
1A-RB'	H ₁₂ -MDI/PTMG(1000)/DMPA/EDA/Dye-1	3:1:1:1:0.2	50.59	49.41
1A-RR'	H ₁₂ -MDI/PTMG(1000)/DMPA/EDA/Dye-2	3:1:1:1:0.2	50.59	49.41
1B	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA	4:2:1:1	39.14	60.86
1B-RB	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA/Dye-1	4:2:1:1:0.2	39.14	60.86
1B-RR	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA/Dye-2	4:2:1:1:0.2	39.14	60.86
1B-RY	H ₁₂ -MDI/PTMG(1000)/DMPA/HEDA/Dye-3	4:2:1:1:0.2	39.14	60.86
2A	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA	3:1:1:1	33.86	66.14
2A-RB	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA/Dye-1	3:1:1:1:0.2	33.86	66.14
2A-RR	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA/Dye-2	3:1:1:1:0.2	33.86	66.14
2A-RY	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA/Dye-3	3:1:1:1:0.2	33.86	66.14
2A-RB'	H ₁₂ -MDI/PTMG(2000)/DMPA/EDA/Dye-1	3:1:1:1:0.2	33.86	66.14
2A-RR'	H ₁₂ -MDI/PTMG(2000)/DMPA/EDA/Dye-2	3:1:1:1:0.2	33.86	66.14
2B	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA	4:2:1:1	24.33	75.67
2B-RB	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA/Dye-1	4:2:1:1:0.2	24.33	75.67
2B-RR	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA/Dye-2	4:2:1:1:0.2	24.33	75.67
2B-RY	H ₁₂ -MDI/PTMG(2000)/DMPA/HEDA/Dye-3	4:2:1:1:0.2	24.33	75.67

^a 1A,1B = PTMG 1000 series; 2A,2B = PTMG 2000 series. A series: component molal ratio of H₁₂-MDI/PTMG(2000)/DMPA/HEDA = 3:1:1:1. B series: component molal ratio of H₁₂-MDI/PTMG(2000)/DMPA/HEDA = 4:2:1:1. RB, RR, and RY: dyed with Remazol (blue), Remazol (red), and Remazol (yellow), respectively.

$$^b \text{Hard-Segment Content (wt \%)} = \frac{\text{H}_{12}\text{-MDI} + \text{DMPA} + \text{HEDA}}{\text{H}_{12}\text{-MDI} + \text{DMPA} + \text{HEDA} + \text{PTMG (1000 or 2000)}}$$

$$^c \text{Soft-Segment Content (wt \%)} = 100\% - \text{Hard-Segment Content.}$$

700–3500 cm⁻¹. The intrinsic viscosity (η_{inh}) was determined with a Cannon type in a constant-temperature water bath at 25°C. Moreover, η_{inh} was calculated as $\eta_{inh} = [\ln(t/t_0)]/C$, where t_0 is the flowing time of the pure solvent, t is the flowing time of the polymer solution, and C is a constant measured at a fixed temperature and with the same solvent (g dL).

The mechanical properties were measured with an Instron model 1122 testing instrument at a cramp rate of 20 mm/min; a paper extension rate of 10 mm/min with a specimen 50 mm long, 10 mm wide, and 0.1–0.2 mm thick; and a full load of 20 kg.

Differential scanning calorimetry (DSC) was performed with a DuPont 2200 at a heating rate of 20°C min under a nitrogen atmosphere to obtain the glass-transition temperature and the melting point.

For the evaluation of the dye migration of dyed PU, the percentage of migration (M_p) was used according to the AATCC test method.¹³ A glass plate, as shown in Figure 1, was coated with the

dyed PU to form a film 0.02 cm thick; region A was covered with a 9-cm-diameter glass cover, but region B was left uncovered. After the temperature was kept at 60°C for 24 h, the diluted dye concentrations of regions A and B in *N*-methyl-2-pyrrolidone (NMP; 10⁻³M) were measured with a photometer.¹³ M_p was calculated as $M_p = [(C_B - C_A)/C_A] \times 100$, where C_A and C_B are the absorbencies of the A and B areas, respectively. Moreover, the colorfastness to water-cooled xenon-arc lamp light was tested according to AATCC test method 16F-1977.

RESULTS AND DISCUSSION

Characteristics of Anionically Modified PU

The codes for all PU dyed and undyed polymer films are shown in Table I. Those marked with a prime were extended with EDA and dyed with a reactive dye.

As shown in Figure 2, the PU films of undyed 1A and 2A and dye-grafted 1A-RB and 2A-RB

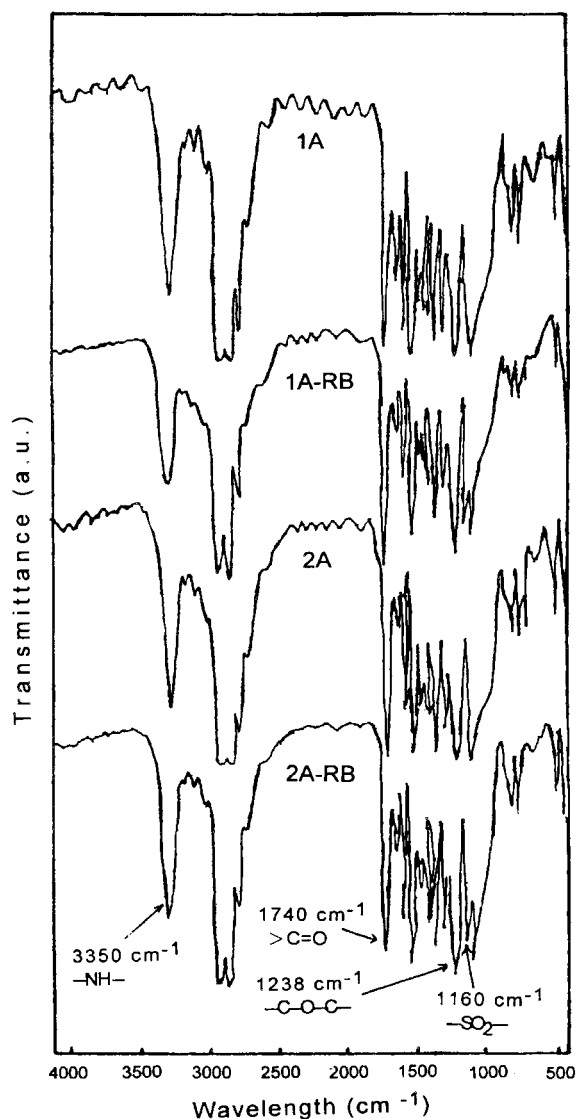


Figure 2 IR spectra of the PU films.

were analyzed with an IR spectrophotometer. The characteristic IR absorption peak of 3350 cm^{-1} demonstrates the —NH— stretching vibration. The characteristic absorption of C=O is observed at 1740 cm^{-1} , >C=O of the urea group is observed at 1640 cm^{-1} , and C—O—C of PTMG is observed at 1238 cm^{-1} . Moreover, the dye-grafted PU film (2A-RB) shows a characteristic absorption peak at 1160 cm^{-1} of the sulfonyl S=O absorption. This demonstrates that the dye was grafted onto the modified PU to form a covalent bond.^{14,15}

Inherent Viscosity (η_{inh}) Analysis

The η_{inh} values of all the polymers are listed in Table II. η_{inh} decreased in the presence of grafted

dye in PU. The decrement of η_{inh} in dye-grafted PU (η_{inh} for 1A = 0.59; η_{inh} for 1ARY = 0.53) is attributed to the decrease in hydrogen bonding (fewer polar groups) and the bulkiness of the dye molecule, which could separate the dye-grafted PU molecule further apart. Therefore, the η_{inh} value of the dye-grafted PU (1ARY) dropped significantly. However, η_{inh} values of 1A and 2A were 0.59 and 0.69, respectively. The value was higher in 2A. This suggests that the PU in the 2A series with PTMG 2000 as the soft segment could produce a higher molecular weight than that in the A1 series with PTMG 1000, resulting in higher intrinsic viscosities. The reason for this is that with the same reactivity of —OH in PTMG, PTMG 2000 with its higher molecular weight produced a higher molecular weight prepolymer than PTMG 1000 as they reacted with $\text{H}_{12}\text{—MDI}$. Consequently, a higher molecular weight for the PTMG 2000 polymer could be obtained.

Thermal Properties of Dye-Grafted PU

The thermal properties of all the types of PU polymers, which were measured by DSC, are shown in Figures 3–6 and are listed in Table III. In Table III, the glass-transition temperatures of the soft segment (T_{gs}) of the 1B or 2B series with lower hard-segment contents show lower values than those of 1A or 2A. This suggests that a PU with a greater content of longer chains of the soft segment could form a greater soft-segment domain, leading to lower values of T_{gs} . However, T_{gs}

Table II η_{inh} Values for All the PU Polymers

Code	η_{inh} (dL/g)
1A	0.59
1A-RB	0.54
1A-RR	0.52
1A-RY	0.53
1B	0.62
1B-RB	0.58
1B-RR	0.57
1B-RY	0.56
2A	0.69
2A-RB	0.62
2A-RR	0.62
2A-RY	0.63
2B	0.72
2B-RB	0.66
2B-RR	0.68
2B-RY	0.68

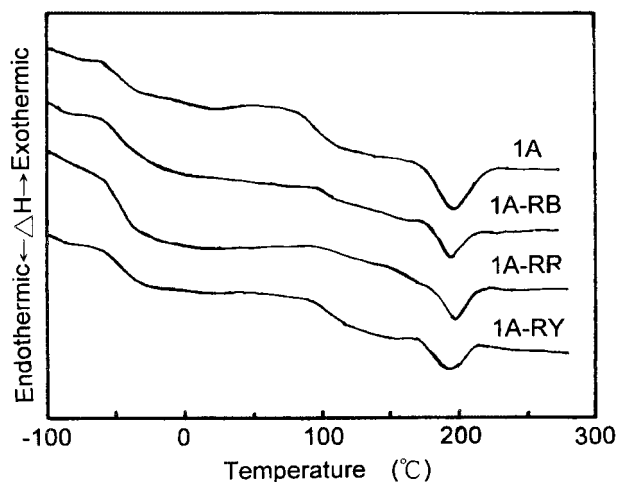


Figure 3 DSC curves of the 1A series PUs.

was not much affected by dye grafting; for example, the T_{gs} values of 1A and 1A-RY were -56.6 and -57.9°C , respectively. This indicates that T_{gs} was not influenced by dye grafting because the dye molecule was not grafted into the soft segment. For the glass-transition temperature of the hard segment (T_{gh}), it is shown in Figure 7 that the dye-grafted PU exhibited a higher value. It is believed that the bulkiness of the grafted dye molecule caused higher steric hindrance and, consequently, a stiffer and higher value of T_{gh} . This result corresponds with the mechanical properties, which were mainly influenced by the hard-segment region. On the basis of these observations, we can conclude that the dye grafted in PU was mostly located in the hard-segment region.

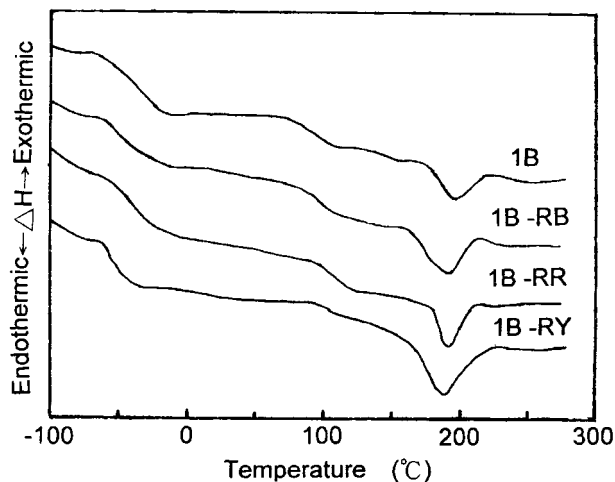


Figure 4 DSC curves of the 1B series PUs.

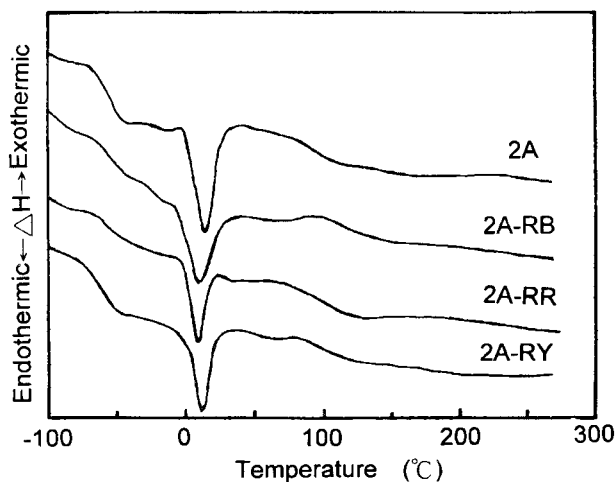


Figure 5 DSC curves of the 2A series PUs.

Also shown in Table III, the melting temperature of the soft segment (T_{ms}) was only seen in those PUs with PTMG 2000, that is, the A2 series. It ranged from 11 to 16.5°C and decreased with an increasing amount of hard segment, but it seemed irregular with the kind of dye grafted. The results of decreasing T_{ms} with the amount of hard segment can be explained by the Flory melting-temperature equation of the copolymer. The PU can be regarded as a copolymer with the hard and soft segments. The melting temperature of the copolymer decreased with the increase in the hard-segment content as a second component. Besides, it is not clearly seen in the DSC figure for the melting temperature of the hard segment (T_{mh}). It is believed that the crystallinity region in the PU was not substantial. As the hard-segment content was less than 38%, T_{mh} did not appear.

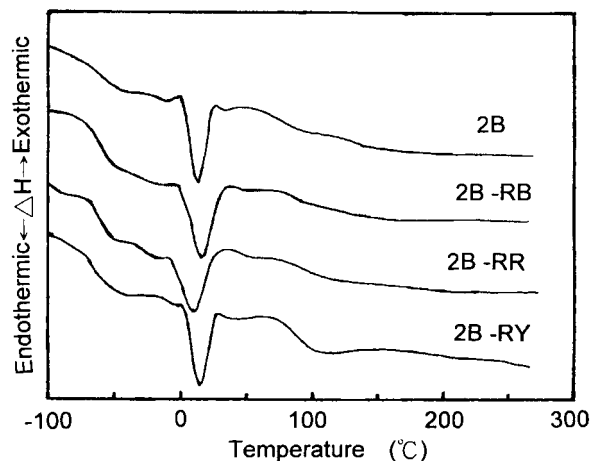


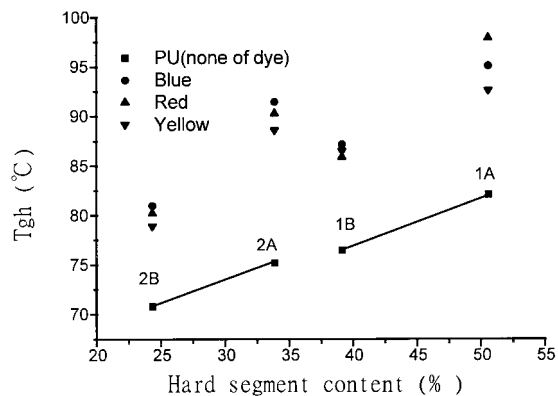
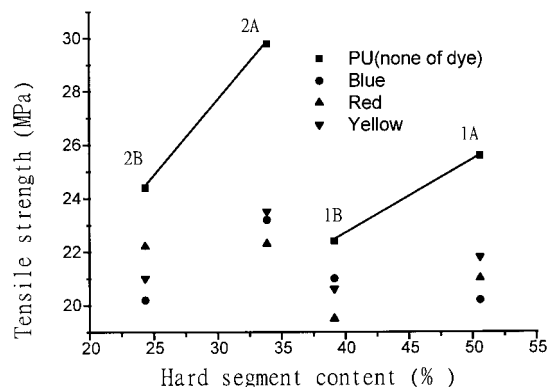
Figure 6 DSC curves of the 2B series PUs.

Table III Thermal Properties of Various PUs

Code	T_{gs} (°C)	T_{ms} (°C)	T_{gh} (°C)	$T_{gh} - T_{gs}$ (°C)
1A	-56.6	—	82.1	139
1A-RB	-57.4	—	95.1	153
1A-RR	-58.3	—	97.9	156
1A-RY	-57.9	—	92.6	151
1B	-59.9	—	76.5	136
1B-RB	-59.2	—	87.2	146
1B-RR	-60.6	—	85.9	147
1B-RY	-60.8	—	86.5	147
2A	-66.2	14.1	75.2	141
2A-RB	-66.7	13.1	91.5	158
2A-RR	-64.0	11.0	90.3	154
2A-RY	-65.6	12.7	88.6	154
2B	-69.7	16.5	70.8	141
2B-RB	-68.8	15.8	81.0	150
2B-RR	-69.5	15.0	80.2	150
2B-RY	-68.5	16.2	78.9	147

Mechanical Properties of Dye-Grafted Anionic PU

The mechanical properties of all the polymers are shown in Figures 8 and 9 and listed in Table IV. Both the initial modulus and the breaking strength decreased in the presence of grafted dye molecules, especially the strength. On the contrary, the breaking elongation increased with the dye molecule. This demonstrated that as the dye molecule grafted in PU, the domain of the hard segment with hydrogen bonding was partially destroyed, and the crystallinity in the hard-segment region consequently decreased. Therefore, both the initial modulus and breaking strength decreased. However, because the amorphous region in dye-grafted PU increased, the breaking elonga-

**Figure 7** Effect of the hard-segment content on T_{gh} for all the PU polymers.**Figure 8** Effect of the hard-segment content on the tensile strength for all the PU polymers.

tion was enhanced. Moreover, as shown in Figure 8, all the mechanical properties increased with the amount of the hard segment. For example, the strengths of 1A and 1B were 25.6 and 22.4 MPa, respectively. The higher value of 1A was due to its harder segment content (50.6%) in comparison with that of 1B (39.1%). Also, as seen in Figure 9, the initial modulus of all the PU polymer increased with the hard-segment content.

Thermal Migration Properties of Dye-Grafted Anionic PU

The results for the dyeing properties of all the dyed PUs are listed in Tables V and VI. PU grafted with a reactive dye did have a better thermal migration property than PU without a dye. Furthermore, those modified PUs dyed with reactive dyes (e.g., 1A-RR) exhibited a better migration property than those with EDA as a chain extender (e.g., 1A-RR'). Therefore, PU with a cova-

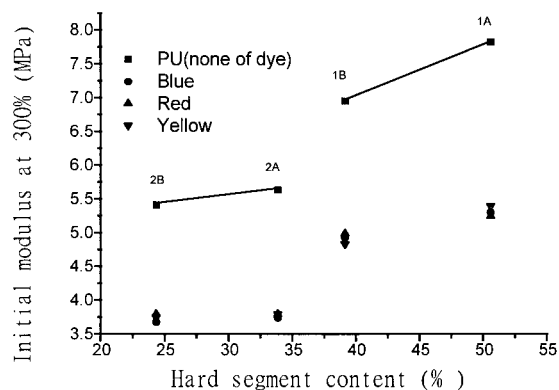
**Figure 9** Effect of the hard-segment content on the initial modulus for all the PU polymers.

Table IV Mechanical Properties of Various PU Polymers

Code	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (MPa) at 300%	Initial Modulus (MPa) at M600%
1A	25.6	350	7.82	—
1A-RB	20.2	380	5.30	—
1A-RR	21.0	390	5.24	—
1A-RY	21.8	390	5.39	—
1B	22.4	420	6.95	—
1B-RB	21.0	460	4.93	—
1B-RR	19.5	470	4.98	—
1B-RY	20.6	470	4.83	—
2A	29.8	610	5.63	4.80
2A-RB	23.2	650	3.74	2.73
2A-RR	22.3	660	3.79	2.69
2A-RY	23.5	660	3.79	2.74
2B	24.1	740	5.41	3.33
2B-RB	20.2	780	3.68	2.21
2B-RR	22.2	780	3.79	2.29
2B-RY	21.0	790	3.74	2.21

lent bond of the dye molecule could contribute to the best thermal migration property. Similarly, for dye colorfastness, it is apparent from Table VI that those PUs with reactive hydroxy groups (e.g., 1A-RR) exhibited better colorfastness than those containing no hydroxy groups (e.g., 1A-RR'). On this basis, we can conclude that the reactive hydroxy groups of PU that could form a covalent bond with the dye molecule contributed to its thermal migration and colorfastness properties.

CONCLUSIONS

In this study, PTMG of two different molecular weights (1000 and 2000), MDI, and HEDA were

Table V Migration Properties of Dye-Grafted PU Films

Code ^a	C_A (10^{-3} g/wg)	C_B (10^{-3} g/wg)	M_p ^b
1A-RB	0.072	0.075	4.17
1A-RR	0.961	0.993	3.23
1B-RB	0.051	0.053	3.92
1B-RR	0.605	0.633	4.63
2A-RB	0.054	0.056	3.70
2A-RR	0.665	0.686	3.16
2B-RB	0.027	0.028	3.70
2B-RR	0.369	0.388	5.15
1A-RB'	0.068	0.079	16.2
1A-RR'	0.869	0.996	14.6
2A-RB'	0.051	0.058	13.7
2A-RR'	0.612	0.705	15.2

^a Prime indicates the use of EDA as a chain extender.

^b $M_p = (C_B - C_A)/C_A \times 100\%$

employed for the synthesis of PU copolymers. Those modified PUs with HEDA as a chain extender were grafted with the reactive dye. From the experimental results, the η_{inh} values of dye-grafted PU decreased, and the tensile strength was lowered, but elongation was enhanced. Also, the dye-grafted PU exhibited a greater value of T_{gh} but showed almost no effect on T_{gs} and T_{ms} . This indicated that the dye was grafted mainly in the hard-segment region of PU. For the dyeing properties, the dye-grafted PU did show better thermal migration and colorfastness properties, indicating that the presence of a covalent bond between the dye and PU could prevent the ther-

Table VI Colorfastness Property of Dye-Grafted PU Films

Code ^a	Light Fastness
1A-RB	5–6
1A-RR	6
1B-RB	4–5
1B-RR	5–6
2A-RB	5
2A-RR	6
2B-RB	6
2B-RR	6
1A-RB'	2
1A-RR'	1–2
2A-RB'	2
2A-RR'	2

^a Prime indicates the use of EDA as a chain extender.

mal migration of the dye and sustain better colorfastness in dyed PU.

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