

# Graft Copolymer of Gelatin / Butyl Acrylate and Its Use in the Dye Transferring Blank Film

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## Synopsis

Butyl acrylate was graft copolymerized onto gelatin using ceric ammonium nitrate as redox initiator. A series of grafted products with various gelatin-to-butyl acrylate ratios were prepared. The molecular weight of the grafted side chains and the number of grafting sites were measured. The possible grafting sites on gelatin macromolecules were pointed out through amino acid analysis. The electron micrograph and DSC analysis showed that the grafted chain (PBA) and backbone gelatin were in separated phases. The graft copolymer was used in the receiving layer of the dye transfer blank film, and the photographic, dye transfer printing, and some physico-mechanical properties were studied with satisfactory results.

## INTRODUCTION

Grafting of vinyl monomers onto gelatin is a means of improving the properties of gelatin. Croome<sup>1</sup> has reviewed the application of graft copolymers in photographic materials. For example, the addition of graft copolymer in color emulsions can improve the mechanical and photographic properties of the emulsion layer.<sup>2</sup> Besides, the graft copolymers can also increase the strength and heat resistance of the light-sensitive film and can decrease its sensitivity to low humidity in surrounding medium.<sup>3</sup>

The graft copolymerization of butyl acrylate (BA) onto gelatin was reported previously.<sup>4</sup> As an extension of that work, further studies were made. In this paper the molecular weight of the grafted side chain and the number of grafting sites were measured. The amino acid analysis was obtained, so as to know the possible grafting sites.

The prepared graft copolymer (gelatin-*g*-PBA) was tried to use in the receiving layer of the dye transfer blank film. Dye transfer blank film is a kind of film used in dye transfer process for making color pictures. It has two layers: the receiving layer and the emulsion layer. The former is used to accept the dye image and the latter to print a black and white silver sound track. During the process of successive transferring dye images from the matrices, the blank film should have enough strength to endure various kinds of forces such as pulling, abrasing, swelling, shrinking, etc. The addition of gelatin-*g*-PBA can increase the elasticity of gelatin film and decrease its shrinkage.<sup>5</sup> Here in this paper more attention is paid to the light-sensitive

properties, dye transfer printing properties, and some other physicochemical properties. The graft copolymers used were in different gelatin-to-BA ratios, and the effect of them on the above properties was studied. This information has not yet been reported in publications so far.

## EXPERIMENTAL

### Preparation and Identification of the Graft Copolymer

The graft copolymerization of BA onto gelatin was carried out in aqueous medium initiated by ceric ammonium nitrate under certain conditions. With different gelatin-to-BA ratios, a series of gelatin-*g*-PBA were prepared. The crude products were Soxhlet-extracted. The graft copolymer was identified by solvent extracting properties and IR spectrum. The procedure in detail and the results were reported in our previous paper.<sup>4</sup>

### Hydrolysis of the Graft Copolymer

The prepared graft copolymer was hydrolyzed with 6*N* HCl in an ampule at 110°C for 24 h. The aqueous part of the hydrolyzed products was subjected to amino acid analysis. The insoluble part which was the grafted PBA side chains was soaked and washed with distilled water for several times, until the wash water did not show any color with ninhydrin reagent. Then the grafted PBA side chains were dried under a vacuum. They were used for the following tests. At the same time, a physical mixture of gelatin and homo-PBA was treated similarly as a contrast test.

### Ninhydrin Test

The soaked and dried insoluble part of the acid hydrolysis and that of the contrast test were dissolved in acetone separately. After the addition of ninhydrin reagent (acetone solution), both solutions were heated, and the color change of them was observed.

### Molecular Weight of Gelatin and Grafted PBA Side Chain

The molecular weight of gelatin was measured by gel permeation chromatography. The molecular weight of the grafted PBA side chains was measured as follows: the soaked and dried PBA side chains obtained after acid hydrolysis were dissolved in acetone to make 0.1% solution (by weight). The intrinsic viscosity of this solution was measured at 25°C by using an Ubbelohde dilution viscometer. The molecular weight of the grafted PBA side chain can be calculated with Mark-Houwink equation<sup>6</sup>:

$$[\eta] = KM^\alpha$$

where  $K = 6.85 \times 10^{-3}$  (mL/g) and  $\alpha = 0.75$

### Determination of the Number of Grafting Sites

From the molecular weight of gelatin and that of the grafted PBA side chains, the average number of grafting sites for a known percentage of

grafting can be calculated as follows:

$$\text{average number of grafting sites} = \frac{(\text{wt grafted PBA})/(\text{mol wt PBA})}{(\text{wt gelatin used})/(\text{mol wt gelatin})}$$

### Amino Acid Analysis

Both gelatin and graft copolymer were acid hydrolyzed, and both of the filtrates were diluted with water and then evaporated under vacuum at 40–50°C to expel HCl thoroughly. The residue was dissolved in water and the pH was adjusted by sodium citrate buffer. This solution was subjected to amino acid analysis using a Hitachi-035 amino acid analyzer.

### Coating of the Dye Transfer Blank Film

The emulsion of graft copolymer (reaction mixture) was added to the coating solution which consisted of gelatin and other additives, and was used as the receiving layer of the blank film. This prepared coating solution, after mixing thoroughly, was overcoated onto the photographic emulsion layer of blank film with the help of a lab coating machine, and then dried at room temperature. After drying, the film should be stabilized for about 1 month to complete the hardening process of the coating layer. Then the prepared film can be subjected to the following tests.

### Measurement of Light-Sensitive Properties of the Film

The prepared blank film was exposed through a step wedge negative on the Kodak sensitometer type 6, and then developed with D-76 at 20°C for 4 min, followed by water washing 2 min, fixing 2 min, and final washing. After drying, a black and white silver positive wedge could be obtained. The densities of every step were measured one by one on a Kodak TD-504 densitometer. From these data, the characteristic curve could be plotted, and the values of  $D_0$  (fog density level),  $D_{14}$  (controlling density), and  $D_{\max}$  (maximum density) were obtained. At the same time, a Kodak film used as the standard and a reference film without grafting copolymer were measured in the same way for comparison.

### Measurement of Dye Transfer Properties of the Film

Three strips of matrix continuous wedge, printed by blue, green, and red light separately, were dyed for 1.5 min with yellow, magenta, and cyan dye solutions respectively. The prepared blank film was prewetted in an aqueous solution of Triton X-100 for 0.5 min. Then on a lab manual dye-transfer machine the dyed matrix was overlaid on the receiving layer of the prewetted blank film and heated for 1.5 min to transfer the dye from the matrix into the blank film. Thus, the dye-printing wedges of yellow, magenta, and cyan were obtained separately. The characteristic curves of them could be plotted with the help of an auto-scanning densitometer. Then the values of  $D_0$  (fog density),  $D_9$  (controlling density), and  $D_{\max}$  (maximum density) were obtained. A Kodak film and a reference film were also measured in the same way for comparison.

### Measurement of Curling Degree, Wetting Property and Transparency of the Film

The prepared blank film was soaked with water for 24 h, and the curling angle was measured under wetted conditions. Then the film was taken out from the water and dried compulsorily with  $\text{CaCl}_2$ . The curling angle under dried conditions was measured as well. Similarly, the curling angles of the wetted and dried blank film without grafting copolymer were measured for comparison.

The wetting angle of the prepared blank film was measured on a contact angle measuring apparatus (JY-82). The wetting agent used was Triton X-100 solution.

The transparency was determined by spectrophotometer at the wavelength of 600 nm.

## RESULTS AND DISCUSSION

### Evidence of Grafting

**IR Spectrum.** The formation of graft copolymer could be proved by IR analysis. The grafting product was Soxhlet-extracted with acetone and hot water thoroughly. The extracted product was free from pure gelatin and homo-PBA; its IR spectrum shows absorption of amide ( $1660, 1550 \text{ cm}^{-1}$ ) due to gelatin and carbonyl ( $1730 \text{ cm}^{-1}$ ) due to PBA. These were reported in our previous paper.<sup>4</sup>

**Ninhydrin Test.** The formation of graft copolymer can be further confirmed through the detection of amino acid end groups in the grafts isolated after acid hydrolysis. When the insoluble part of the graft copolymer was treated with ninhydrin reagent, the characteristic purple blue color appeared, which was associated with the presence of amino acids. In the case of a physical blend of homo-PBA and gelatin, the residue obtained after acid hydrolysis did not give any color with ninhydrin. These results indicated that the end groups of the grafted chains were amino acid residues. This further confirmed that between the polypeptide chain of gelatin and PBA, chemical bonds had existed, i.e., actual grafting of PBA to gelatin had occurred.

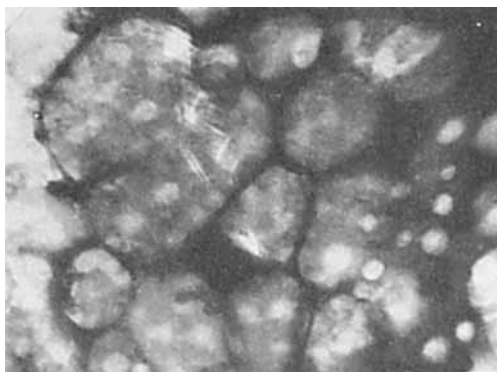


Fig. 1. TEM photo of gelatin-*g*-PBA film stained with 2% phosphotungstic acid: 100 KV,  $34,000\times$ .

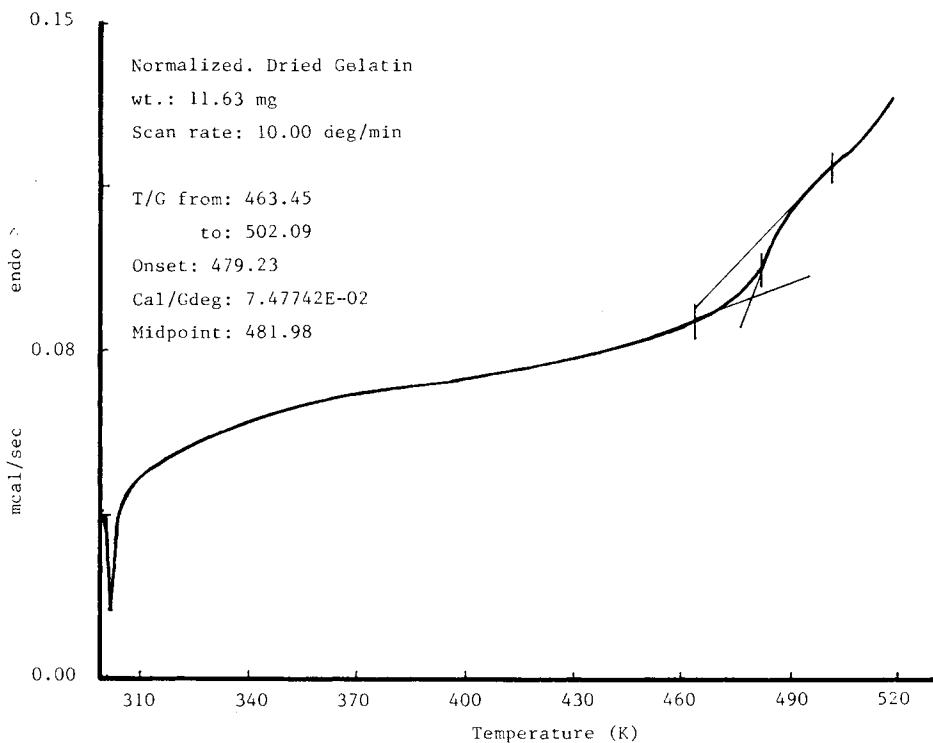


Fig. 2. DSC of dried gelatin.

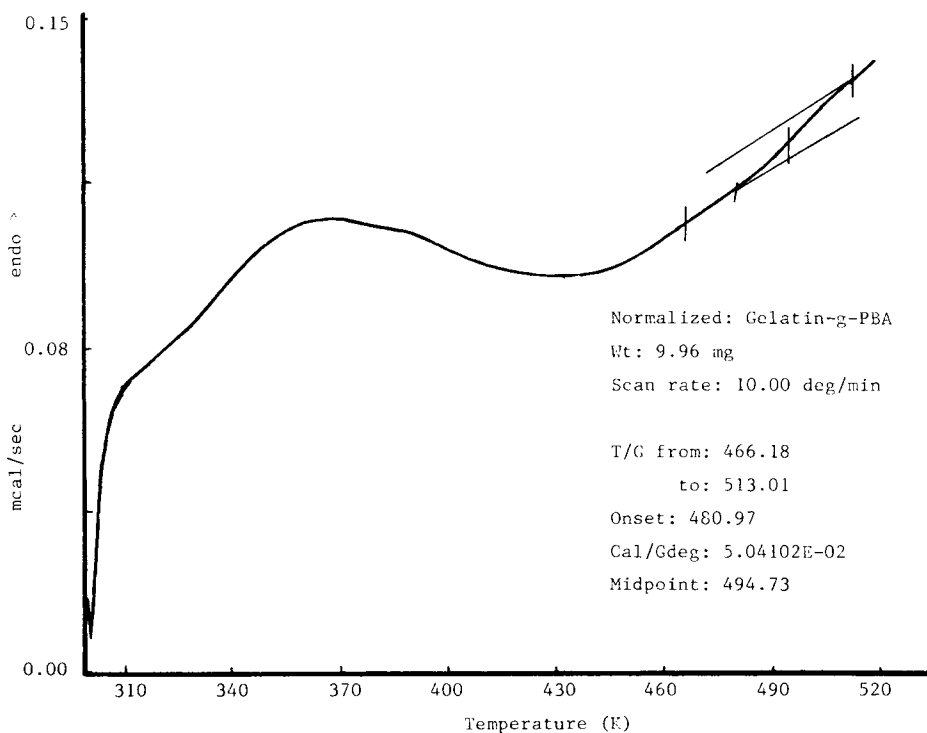


Fig. 3. DSC of gelatin-g-PBA.

### The Microstructure of the Graft Copolymer

A thin film of the graft copolymer was made from its cresol solution. The film was dyed with 2% phosphotungstic acid solution (pH = 7), and photographed through TEM. Figure 1 is the TEM photo of gelatin-*g*-PBA. The dark parts in the photo are the gelatin phase, while the light parts are the PBA phase. This indicates that the backbone (gelatin) and side chain (PBA) existed in separated microphases. This fact was also demonstrated by the differential scanning calorimetry. The DSC results are shown in Figures 2 and 3. The glass-transition temperature of dried gelatin was at the range of 463–502 K (Fig. 2) and that of graft copolymer was 466–513 K (Fig. 3). This indicates that the glass transition temperature range of gelatin is not changed by the grafting of PBA side chains; i.e., the gelatin backbone and PBA side chains were in separated phases.

### The Molecular Weight of Gelatin

The molecular weight of gelatin used was determined by the gel permeation filter method; the results are shown in Figure 4, in which

$$M_w = 132,000, \quad M_n = 103,000, \quad d = 1.28$$

including

$M_w > 200,000$	16%
$M_w = 100,00-110,000$	14%,
$M_w = 90,000-100,000$	10%
$M_w < 50,000$	3%
$M_w = 80,000-130,000$	41%

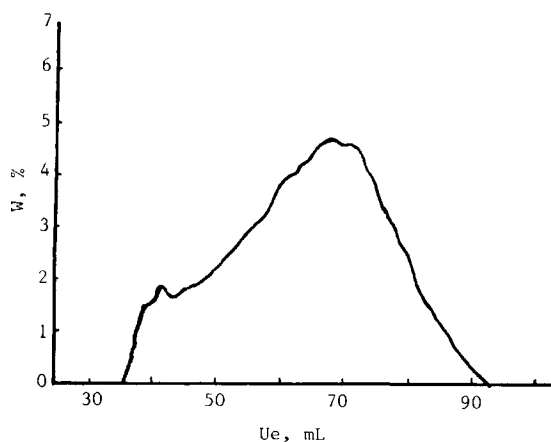


Fig. 4. The elution curve of gelatin: column, 10 × 1000 mm, filled with Sepharose 4B; gelatin concentration, 0.4% (in 0.4M NaCl); sample amount, 0.25 mL × 4 mg/mL = 1 mg; eluting solution, 0.2M NaCl; flowing rate, 9–10 mL/h; fractional volume, 1.5–1.6 mL; detecting wavelength, 230 nm; standards for calibration, very narrow distribution  $\alpha$ ,  $\beta$ ,  $\gamma$ , and other gelatin components of known molecular weights were used for calibration.

TABLE I  
Factors Influencing the Molecular Weight of the Side Chains

No.	Factors		$[\eta]$ (mL/g)	$\bar{M}_w$ of PBA side chains	Other conditions
1	[CAN] $10^3$ (mol/L)	3.648	4.04	4936	[Gel] = $1.515 \times 10^{-4}$ (mol/L), [BA] = 0.351 (mol/L), [HNO <sub>3</sub> ] = 0.04 (mol/L), temp = 40°C, time = 20 min
		7.297	3.20	3625	
		9.121	1.90	1809	
2	[BA] (mol/L)	0.260	3.57	4194	[Gel] = $1.515 \times 10^{-4}$ (mol/L), [CAN] = $3.648 \times 10^{-3}$ (mol/L), [HNO <sub>3</sub> ] = 0.04 (mol/L), temp = 35°C time = 20 min
		0.351	4.30	5375	
		0.456	4.85	6310	
3	Temp (°C)	35	3.65	4320	[Gel] = $1.515 \times 10^{-4}$ (mol/L), [BA] = 0.351 (mol/L), [CAN] = $7.297 \times 10^{-3}$ (mol/L), [HNO <sub>3</sub> ] = 0.04 (mol/L), time = 20 min
		40	3.20	3625	
		45	3.17	3580	
		50	2.73	2933	

### The Molecular Weight of Grafted Side Chains and the Number of Grafting Sites

The molecular weight of grafted side chains was determined by viscosity method. A series of results were listed in Table I. These experiments were made for observing the effects of initiator concentration, monomer concentration, and reaction temperature on the molecular weight of side chains. It can be seen that, in the system studied, the molecular weight of the side chains are within the range of 3000–6000. They increased with the increasing of monomer concentration and decreased with increasing initiator concentration and raising temperature. Therefore, it is possible to adjust the molecular weight of side chains by varying the above factors.

The average number of grafting sites was calculated by using eq. (2). The effects of initiator concentration, monomer concentration, and reaction temperature on the number of grafting sites were listed in Table II.

From these data, it was found that, controlling the reaction conditions and the percentage of grafting (PG) could adjust the number of grafting sites. In the system studied here, the number of grafting sites were within 10–20 mol PBA/mol gelatin. The larger number of grafting sites indicated that the grafted chains are shorter.

### Amino Acid Analysis of Graft Copolymer

In order to approach the grafting locations on the gelatin molecules, the amino acid analysis was made. The amino acid compositions of the grafted and ungrafted gelatin were shown in Table III. Comparing the amino acid compositions of these two samples, it could be found that the contents of threonine, isoleucine, leucine, phenylalanine, and arginine in the graft copolymer showed a significant decrease. These results, therefore, indicate that the above amino acids may be involved as the grafting sites. Besides, it is

TABLE II  
Factors Influencing the Number of Grafting Sites

No.	Factors	PG (%)	Number of grafting sites (mol/mol)	Other conditions	
1	[CAN] × 10 <sup>3</sup> (mol/L)	3.648	113.24	30.2	[Gel] = 1.515 × 10 <sup>-4</sup> (mol/L), [BA] = 0.351 (mol/L), [HNO <sub>3</sub> ] = 0.04 (mol/L), temp = 40°C, time = 20 min
		7.297	169.84	61.8	
		9.121	164.21	119.8	
2	[BA] (mol/L)	0.260	38.81	12.2	[Gel] = 1.515 × 10 <sup>-4</sup> (mol/L), [CAN] = 3.648 × 10 <sup>-3</sup> (mol/L), [HNO <sub>3</sub> ] = 0.04 (mol/L), temp = 35°C, time = 20 min
		0.351	62.29	15.3	
		0.456	70.86	14.8	
3	Temp (°C)	35 <sup>a</sup>	130.73	40.0	[Gel] = 1.515 × 10 <sup>-4</sup> (mol/L), [BA] = 0.351 (mol/L), [CAN] = 7.297 × 10 <sup>-3</sup> (mol/L), [HNO <sub>3</sub> ] = 0.04 (mol/L),
		40 <sup>a</sup>	169.84	61.9	
		45 <sup>b</sup>	143.87	53.1	
		50 <sup>b</sup>	178.57	80.4	

<sup>a</sup>time = 20 min,

<sup>b</sup>time = 10 min

TABLE III  
The Amino Acid Analysis of Pure Gelatin and the Graft Copolymer

Amino acids	Content (residues/1000 total residues)	
	Pure gelatin	Graft copolymer
Aspartic acid	5.3	12.5
Threonine	55.2	17.3
Serine	30.4	40.8
Glutamic acid	80.2	108.4
Glycine	386.4	384.0
Alanine	147.0	141.6
Cystine	1.7	0
Valine	27.1	26.1
Methionine	0.2	0.6
Isoleucine	9.4	1.9
Leucine	20.0	2.5
Tyrosine	0	0
Phenylalanine	9.9	5.5
Ornithine	2.6	9.12
Lysine	31.8	33.1
Histidine	2.4	6.0
Tryptophane	0	0
Arginine	57.1	38.6
Proline	131.6	172.0



interesting to note that the contents of serine, glutamic acid, and proline in the graft copolymer increased obviously. The cause of the increase is not clear yet. George et al. have reported the amino acid analysis of gelatin-g-PBA (prepared in water-isopropanol medium, initiated by  $K_2S_2O_8$ ).<sup>7</sup> Although the composition they made is not exactly the same as our data, the significant decrease in threonine and the increase in proline are similar.

### Light-Sensitive Properties

The prepared graft copolymers were added to the receiving layer emulsion of the blank film, and coated on the film as mentioned above. The light-sensitive properties of the film samples were measured, and the obtained fog density level ( $D_0$ ), controlling density ( $D_{14}$ ), and maximum density ( $D_{max}$ ) are listed in Table IV.

In this table, samples I, II, III, IV, V represent the graft copolymers used with different gelatin-to-BA ratios. The obtained data showed that different graft copolymers and different amount added did not give any significant influence in  $D_0$  and  $D_{max}$ . As for the controlling densities ( $D_{14}$ ), they were kept within the range between those of the standard and the reference films. Therefore, it can be concluded that the addition of prepared graft copolymer

TABLE IV  
Light-Sensitive Properties of the Testing Samples

Samples	Amt. added (wt %) <sup>a</sup>	$D_{max}$	$D_{14}$	$D_0$
Standard	0	4.13	1.51	0.06
Reference	0	4.11	1.93	0.08
I <sup>b</sup>	10	4.14	1.51	0.05
	20	4.36	1.67	0.05
	30	3.97	1.54	0.05
	40	—	—	—
	II	10	3.85	1.85
	20	4.22	1.88	0.06
	30	3.61	—	0.05
	40	3.65	1.40	0.06
III	10	4.02	1.61	0.06
	20	4.05	—	0.05
	30	4.25	1.72	0.07
	40	4.15	1.67	0.12
IV	10	3.80	1.33	0.06
	20	4.02	1.72	0.05
	30	—	—	—
	40	4.08	2.04	0.05
V	10	4.36	2.07	—
	20	4.02	2.13	—
	30	4.03	1.71	0.06
	40	4.03	1.86	0.06

<sup>a</sup>Amount of graft copolymer added.

<sup>b</sup>The gelatin-to-BA ratios of samples I-V are: 1:0.67, 1:1, 1:1.33, 1:2, and 1:2.67 (by wt.), respectively. The other conditions for preparing the graft copolymers are:  $[Gel] = 1.14 \times 10^{-4}$  (mol/L),  $[CAN] = 5.47 \times 10^{-3}$  (mol/L),  $[HNO_3] = 0.04$  (mol/L),  $[OP-10] = 0.2\%$ , temp = 40°C, time = 4 h.

TABLE V  
Dye Transfer Properties of the Testing Samples

Samples <sup>a</sup>	Amt. added (wt %) <sup>b</sup>	Yellow			Magenta			Cyan		
		$D_{\max}$	$D_9$	$D_0$	$D_{\max}$	$D_9$	$D_0$	$D_{\max}$	$D_9$	$D_0$
Standard	0	3.76	—	0.00	4.20	—	0.04	3.64	—	0.06
Reference	0	3.65	1.80	0.04	4.00	1.60	0.00	3.58	1.00	0.04
I	10	3.50	1.82	0.38	3.90	1.60	0.02	3.26	1.23	0.04
	20	3.78	1.86	0.42	3.88	1.56	0.02	3.88	1.30	0.04
	30	3.70	1.76	0.36	3.40	1.50	0.02	3.76	1.22	0.02
	40	—	—	—	4.00	1.60	—	—	—	—
II	10	3.74	1.70	0.47	4.10	1.60	0.08	3.80	1.35	0.02
	20	3.61	1.68	0.38	3.86	1.48	0.01	3.68	1.40	0.10
	30	3.66	1.90	0.39	—	—	—	3.67	1.20	0.10
	40	3.65	—	—	3.30	1.44	0.06	3.80	0.94	0.04
IV	10	3.67	1.86	0.42	4.00	1.50	0.00	3.92	1.23	—
	20	3.63	1.82	0.40	4.20	1.62	0.02	3.76	1.20	0.03
	30	3.69	1.73	0.42	4.20	1.44	0.04	3.92	0.98	—
	40	3.07	1.84	—	4.02	1.42	0.01	3.60	1.14	0.04
V	10	3.72	1.66	0.38	4.30	—	0.04	3.89	1.18	0.05
	20	3.30	1.98	0.30	4.20	1.62	0.02	3.64	1.35	0.12
	30	3.31	1.50	—	4.06	1.46	0.02	3.85	1.22	0.04
	40	3.10	1.49	—	3.56	1.44	0.05	3.36	1.24	0.02

<sup>a</sup>The data for III are omitted.

<sup>b</sup>Amount of graft copolymer added.

into receiving layer will not alter the light-sensitive properties of the blank film.

### Dye Transfer Properties

The dye transfer properties of the testing samples were evaluated according to the dye printing characteristic curves obtained by transferring dye images from the wedge matrices dyed with yellow, magenta, and cyan, respectively. From these printing characteristic curves, the  $D_{\max}$ ,  $D_9$ , and  $D_0$  of different testing samples can be obtained and are listed in Table V. It can be seen that the addition of graft copolymer into the receiving layer gave no bad effect on the dye transfer properties of the blank film except enhancing the yellow fog level ( $D_0$ ). But this can easily be removed and corrected by the washback technique in the mass production.

### Other Properties

In order to get a good quality of dye transfer printing picture with high definition and clearness, it is important for the blank film to possess perfect transparency, good prewetting property, and dimensional stability. Some results were listed in Table VI, which can partially reflect the above properties. It is apparent that the surface wetting angles increased with the increasing amount of graft copolymer added. This might lead to lower the prewetting behavior of the blank film. Such a disadvantage can be overcome by using hydrophilic monomer to copolymerize with butyl acrylate.

TABLE VI  
Some Physicomechanical Properties of the Testing Samples

Samples	Amt. added (wt %) <sup>a</sup>	Wetting angle (°)	Transparency (%) ( $\lambda = 600 \text{ nm}$ )	Curling angle (°)		
				$\theta_{t=0}$	$\theta_{t=\infty}$	$\Delta\theta$
Reference	0	86	92.8	13	20	7
I	10	81	89.5	9	6	-3
	20	85	87.3	11	13	2
	30	98	87.2	—	—	—
	40	108	88.1	—	—	—
II	10	81	88.1	13	7	-6
	20	85	88.5	—	—	—
	30	98	88.2	9	9	0
	40	108	88.5	—	—	—
III	10	82	87.7	9	14	5
	20	—	86.2	—	—	—
	30	96	86.0	—	—	—
	40	98	86.5	8	8	0
IV	10	84	87.3	9	8	-1
	20	99	87.0	5	1	-4
	30	104	87.8	10	8	-2
	40	—	88.0	—	—	—
V	10	90	88.4	5	7	2
	20	94	86.2	—	—	—
	30	106	85.8	8	10	2
	40	100	89.1	8	5	-3

<sup>a</sup>Amount of graft copolymer added.

From Table VI it also can be seen that the addition of graft copolymer did not affect the transparency of the blank film, and the dimensional stability of the film was significantly improved by decreasing its moisture deformation.

The above preliminary results show that the gelatin-*g*-PBA is undoubtedly in favor of improving some physicomechanical properties of the gelatin layer. It can be considered to be used not only in the blank film, but also in other types of light-sensitive materials.

## CONCLUSIONS

The prepared gelatin-*g*-PBA was further identified by ninhydrin test. The molecular weight of the grafted PBA side chains was about 3000–6000, and the average number of grafting sites was within the range 10–120 (mol PBA/mol gelatin). The possible grafting sites on the gelatin macromolecules were proposed.

The addition of the graft copolymer into the receiving layer of dye transfer blank film was made. The light-sensitive properties, dye transfer printing properties, and transparency are not affected by the graft copolymer. The dimensional stability was improved. It can be considered to be used in the dye transfer blank film and other light-sensitive materials.

### References

1. R. J. Croome, *J. Photogramm. Sci.*, **30**, 181 (1982).
2. U. S. Pat. 2,831,767 (1958), Kodak.
3. I. M. Fridman, G. I. Burdygina, E. A. Zimkin, and T. M. Moshikina, *Vysokomol. Soedin.*, **A12**, 1886 (1970).
4. Z. C. Li, Z. F. Fu, M. Z. Huang, and N. Lian *J. Macromol. Sci. Chem.*, **A25**(12), 1487-1513 (1988).
5. L. M. Yarysheva, M. Z. Averbukh, N. F. Bakeev, and P. V. Kozlov, *Vysokomol. Soedin.*, **A16**, 1807 (1974).
6. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., New York, Wiley, 1975.
7. A. George, G. Radhakrishnan, and K. T. Joseph, *Polymer*, **26**, 2064 (1985).

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