

GRAFTING OF ACRYLONITRILE TO POLYPROPYLENE FILMS BY THE USE OF ULTRAVIOLET IRRADIATION

Kiyochika Y_AHIKOZAWA & Takataro SUDA

*Laboratory of Synthetic Textile Chemistry, Faculty of
Textile Science and Technology, Shinshu University*

INTRODUCTION

Polypropylene is difficult to dye and still this fact has seriously limited the use of this polymer, especially in the textile field. Therefore, various methods¹⁻³⁾ are attempted to improve it dyeable and these results are reported in the literature. The technique of radiation grafting among these is one of the interesting methods.⁴⁻⁵⁾ As well shown in general, the irradiation method can be classified into two cases: high energy irradiation and low energy irradiation. The latter method usually requires the use^{6,7)} of a photosensitizer. Each method can be divided as follows: simultaneous grafting and preirradiation method. The preirradiation method can be subdivided into two cases: irradiation in air and irradiation in vacuo.

Among the above methods, studies on grafting of acrylonitrile onto polypropylene films by ultraviolet preirradiation in vacuo and simultaneous irradiation in vapor phase of the monomer, are performed. The reasons why acrylonitrile monomer is used for are as follows. (a) It possesses the ability to swell polypropylene permitting good penetration. (b) The $-C\equiv N$ group is reactive and has a function as a dye-site, or can be reacted with a nucleophilic reagent. In order to be easily done the consideration of experimental results, polypropylene is used as a film.

As to studies on grafting of acrylonitrile onto polypropylene by the irradiation method, A. Chapiro⁸⁾ has found that polymer peroxides are formed in polypropylene during high energy irradiation in air and these peroxides, when heated in the presence of a monomer, are decomposed and initiate the polymerization of the monomer, forming a graft copolymer. H. Sobue, et al⁹⁾ have reported the results of a kinetic investigation on the grafting of acrylonitrile onto polypropylene films by a preirradiation method in air. It is described in a patent¹⁰⁾ that the $-C\equiv N$ group in the graft copolymer prepared by a ultraviolet irradiation is treated with hydroxylamine or hydrazine and these derivatives, and that dyeability of treated graft copolymer is greatly increased with respect to acid dyes.

The present work is aimed to study the effects of various factors such as kind of photosensitizer, photosensitizer concentration, grafting time, grafting temperature and dose rate by the above method. Dyeability and

physical properties of grafted polypropylene films are also studied.

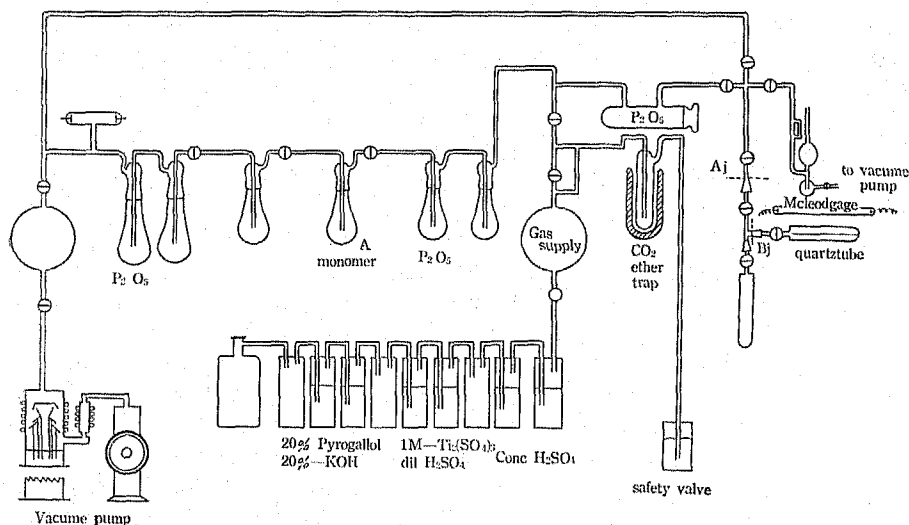
EXPERIMENTAL PROCEDURE

Materials

Polypropylene powder, obtained from Avisun Company, was used as sample. The film (thickness, 0.027 mm) was prepared by extruding the molten polypropylene in nitrogen, cut off in a rectangular form with a size of 3.5×3.0 cm on a section paper, extracted with ether¹¹⁾ in a Soxhlet extractor for about 8 hrs. to remove stabilizers, dried under reduced pressure, and weighed. The films were then loaded with this sensitizer in benzene at room temperature, warming to drive off all solvent. The sensitizer content of a film was also adjusted by changing the sensitizer concentration of soaking solution. Acrylonitrile monomer was distilled after washing with mild acid and alkali as any inhibitors are not present.

Irradiation and Grafting

The graft copolymerization by ultraviolet irradiation method was carried out by using one of various modifications of the apparatus shown in Fig. 1a~1b. The apparatus for removing oxygen was flushed with the purified nitrogen before evacuating. The procedure was repeated twice. The films for irradiation were placed on a glass frame (31×160mm) in a quartz tube (40×200mm). The quartz tube containing films was evacuated to 1×10^{-4} mm Hg. The stopcock A was then closed. Irradiation was performed in light source of different dose rates. Distilled monomer was added to flask A. The flask containing the monomer was evacuated by two freezing-pumping-thawing cycles using a vapor pump. The stopcocks, B, C were closed. The entire system was again evacuated to 1×10^{-4} mm Hg. The ample supply of



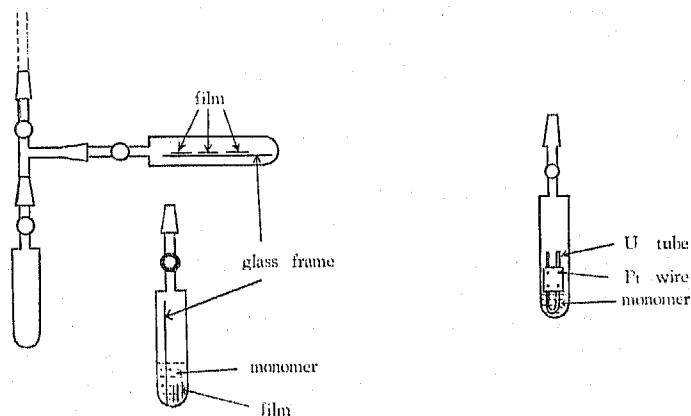


Fig. 1-a apparatus for irradiating polypropylene in controlled atmosphere.

monomer to immerse the irradiated film was admitted to tube 1 cooling with a dry-ice and ether mixture bath from flask A. The stopcock D was closed. The entire system was divided at the joint Aj. The stopcock A was opened. The monomer was then transferred from tube 1 to the quartz tube immersing the irradiated film. The quartz tube was further more separated at the joint Bj. The graftpolymerization reactions were carried out under the definite condition.

In the case of the simultaneous irradiation shown in Fig. 1-b, the film for irradiation is fitted on U-tube by the platinum wire in the quartz tube. The monomer was added to the quartz tube containing a film in vacuo. The apparatus shown in Fig. 1-a. was used in adding. The grafting reaction was carried out under the definite condition.

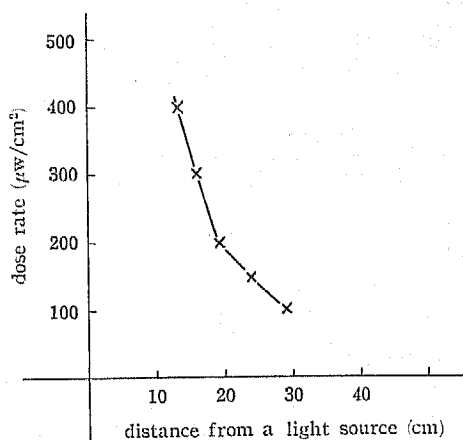


Fig. 2 The variation of dose rate as a function of a distance from the light source.

Toshiba GH-601 B 6 W low pressure mercury vapour lamp, was used as the light source, since about 95% of their wave length is $253.7 \text{ m}\mu$. All irradiations were performed under vacuo with room temperature. The light intensity received in the sample film was measured by the illuminometer. The variation of dose rate as a function of a distance from the light source was shown in Fig. 2.

Determination of Per Cent Grafting

After the graft reaction, the films were removed from the monomer, immersed in a large volume

of dimethylsulfoxide at 60°C in order to extract a large amount of polyacrylonitrile homopolymer, then soaked in metanol, and dried under reduced pressure until constant weight. The amount of grafted monomer was taken to be equal to the measured increase in weight. The per cent grafting is defined as a ratio of the increased weight to the original trunk polypropylene weight.

Mechanical and Physical Testing

Swelling — The grafted films were immersed in dimethylsulfoxide or carbontetrachloride at 110°C or 75°C for 4 hrs., and wiped the excess solvent by the filter paper. The degree of swelling was determined immediately by noting the increase of a film in weight or in length. The swelling per cent calculated respectively from the two equation;

$$S_w, \% \text{ swelling} = \frac{\text{weight of equilibrated film} - \text{initial weight}}{\text{initial weight}} \times 100$$

$$S_l, \% \text{ swelling} = \frac{\text{length of equilibrated film} - \text{initial length}}{\text{initial length}} \times 100$$

Melting Point — Melting point was determined by the micro type melting point determinator, and a slow heating procedure was used, namely 2°C/min. before melting, 1° C/min. during melting, and 2°C/min. after melting.

Tensile Strength and Per Cent Elongation — Tensile strength and elongation of the grafted films were measured with the K-S type senimeter at 20°C.

The thickness of each film was calculated from the weight per its unit area and its specific gravity measured by the ups and downs method. The thickness was also measured under the microscope, and the thickness measured by the former method coincided with that of the latter. The film was cut test pieces of 1 mm in width on a section paper, and these pieces were pasted on a paper frame in the cutting order. The paper frame was cut one by one into test pieces when measured.

Dyeing method and Related Tests

Dyeing — Dyes used were disperse dyes, basic dyes, cationic dyes and acid dyes. The composition of the dye bath is shown in Table 1.

Table 1 Composition of Dye Bath

	Disperse dyes	Basic dyes	Cationic dyes	Acid dyes
dye	4 %	4 %	4 %	4 %
Peletex E421	3	3	3	—
Acetic acid	—	1	1	3.5
Sodium acetate	—	—	2	—

Per cent for the film weight; Liquor length 1:60.

The dyeing was achieved by immersing the films in a dye bath at about 40°C and subsequently bringing the bath to boil for 40 min. and boiling for 60 min. The dyed films were boiled in 0.1% Monogen solution for 15 min. and dried.

Amination — Amination of the $-C\equiv N$ group in the grafted polyacrylonitrile was performed by the following two methods^{12,13} :

(1) The grafted films were treated with 0.25% hydroxylamine HCl and sodium hydroxide in liquor length 1:20 at 100°C for over night. The amount of sodium hydroxide was just sufficient to neutralise half the hydroxylamine HCl.

(2) The grafted films were treated with 0.1 M lithium aluminum hydride-ether solution, in liquor length 1:20 at room temperature for over night then the products were hydrolyzed by immersing in water.

Fastness — Fastness to light was determined by observing films which exposed in the Acme type fademeter for 5 or 10 hr. To determine fastness to washing; the films were treated aqueous solution content of 0.2 wt-% Na_2CO_3 and 0.5 wt-% soap at 70°C for 45 min. The degree of fastness was approximately determined by visual judgment.

Results and Discussion

(1) Grafting

Effect of Sensitizer — Even in the case of non use of sensitizer polyacrylonitrile was grafted onto polypropylene by ultraviolet light, however the amount of grafting in the case of same intensity of ultraviolet light increased enormously when sensitizer was present in the basic plastic, as showed in Fig. 3.

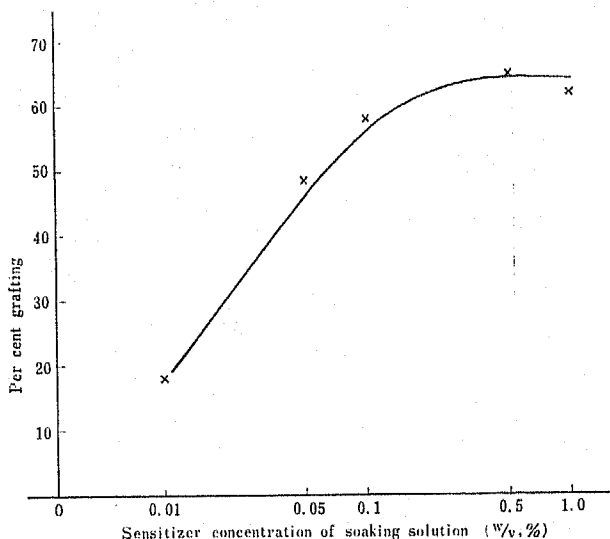


Fig. 3 Per cent grafting as a function of sensitizer concentration, dose rate $200 \mu\text{w}/\text{cm}^2$, grafting temperature 40°C, grafting time 1hr.

A comparative study of several compounds indicating the ultraviolet absorption was carried out to determine the effective sensitizers for this

Table 2 Per cent grafting using various sensitizers
(Same grafting conditions as Fig. 3)

Sensitizer	Molar extinction coef. ($\times 10^4$) at 254m μ	Grafting %	
		Sensitizer concentration in soaking solution	
		10 ⁻³ mole/l	10 ⁻² mole/l
	(metanol)		
Benzophenone	1.97	44	62
Anthraquinone	4.56	36	58
β -Cl-anthraquinone	4.43	2	6
β -NO ₂ -anthraquinone	3.98	0	0
β -CH ₃ -anthraquinone	4.31	2	5
β -NH ₂ -anthraquinone	1.27	0	0
P-quinone	2.59	0	0
Alizaline	2.25	0	0
No sensitizer	—	5	—

grafting reaction and the results were showed in Table 2. Both benzophenone and anthraquinone were found to be effective as sensitizer.

In Fig. 3 is illustrated the effect of increasing the benzophenone content in a film. This was carried out by soaking the samples in various benzene solutions of benzophenone at room temperature for 10 minutes. The benzo-

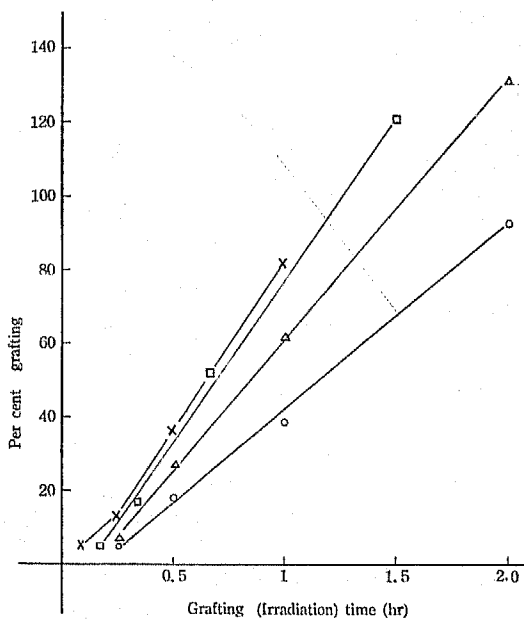


Fig. 4 Effect of dose rate and grafting time in grafting

phenone amount in a film (% w/w) was calculated from the concentration of benzophenone in methanol (5.5×10^{-4} mole per liter at 254 m μ). The per cent grafting obtained as a function of benzophenone content of the films are given in Fig. 4. At the higher benzophenone contents, the per cent grafting becomes rather insensitive to the sensitizer concentration and reaches a maximum of 65% grafting for 0.12-0.45% sensitizer concentration. The sensitizer concentration of about 0.1-0.5%, w/w gave a useful degree of grafting. The same trend was observed in the case of preirradiation. This value is in agreement with the data of 0.25%¹⁴) for grafting and crosslinking. Most of this studies were carried out using a film content of 0.1%, w/w benzophenone.

Simultaneous Irradiation — The variation of the per cent grafting as a function of grafting time is shown in Fig. 5, where the grafting temperature was 40°C and the irradiation dose were 100, 200, 300 and 400 $\mu\text{w}/\text{cm}^2$. It is obvious that the per cent grafting as a function of grafting time between

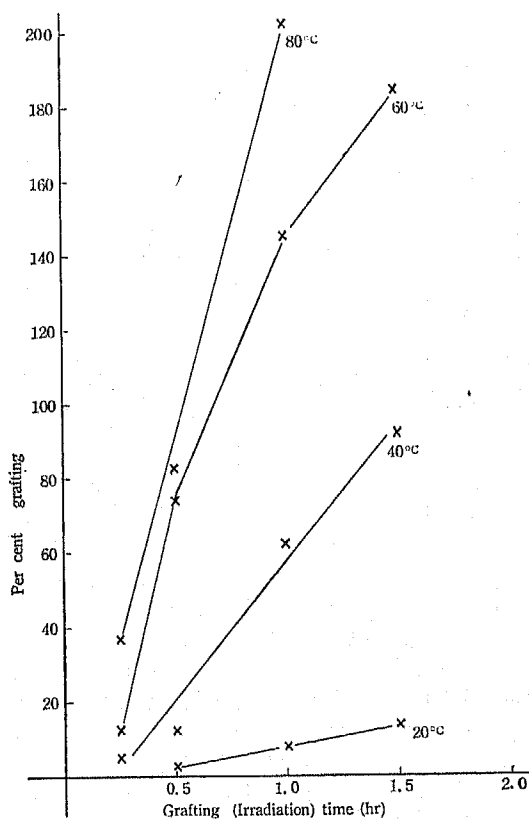


Fig. 5 Effect of grafting temperature and grafting time in grafting

the dose rate, 300 and 400 $\mu\text{W}/\text{cm}^2$ differentiate scarcely. So this fact indicates that in the case of dose rate 400 $\mu\text{W}/\text{cm}^2$, homopolymer producing inside of the quartz tube interferes with the grafting reaction.

The effects of the grafting temperature and time, are shown in Fig. 5. The per cent grafting increase becomes remarkably with the high temperature. This seems to be due to the fact that the vapor pressure of monomer and the rate of reaction increase at high temperatures.

Fig. 6 shows the logarithm of hourly grafting rate as function of the reciprocals of absolute temperature.

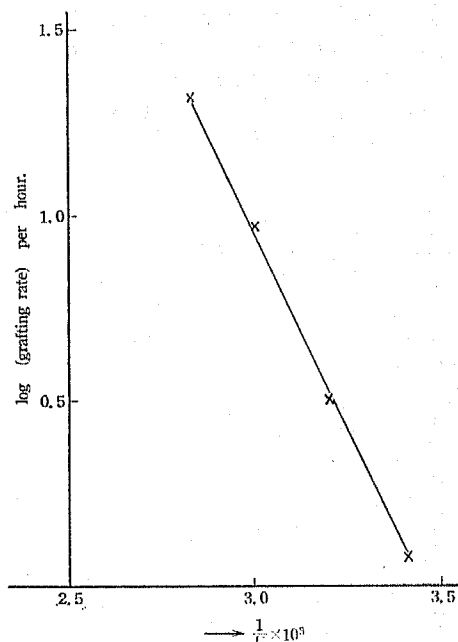


Fig. 6 Grafting rate as a function of reciprocal of absolute temperature.

$$\left(\text{Grafting rate} = \frac{\text{final film weight} - \text{initial film weight}}{\text{initial film weight}} \right)$$

According to the results of Fig. 5, the apparent activation energy of overall reaction was calculated to be 10.7 Kcal. in this range 20–80°C. This value agrees almost with the data of H. Sobue et al. The experiment was difficult owing to produce remarkably the homopolymer inside of the quartz tube, where the grafting temperature is above 100°C. The simultaneous irradiation technique has a weak point that a greater amount of homopolymer than in the case of preirradiation occurs, but may make easily the high grafted films. As will be discussed below, the preirradiation technique that the excessive homopolymer can be limited, was carried out also.

Effect of Dose Rate, Grafting Temperature and Grafting Time — It is widely¹⁵⁾ known that the physical property of polypropylene is ultimately degraded by ultraviolet irradiation. Fig. 7 shows the changes in the physical properties of polypropylene films after different irradiation times with a Toshiba GH-601 B lamp at a distance of 13.8 cm between sample and lamp in

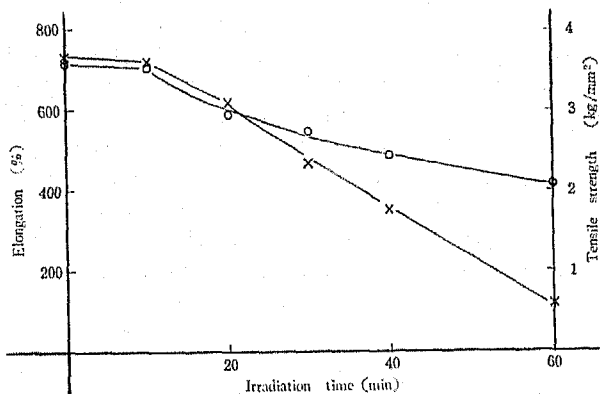


Fig. 7 Variation of tensile strength and elongation as a function of irradiation time.

○ Tensile strength, × elongation.

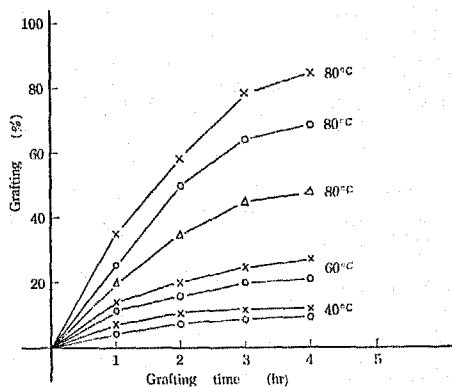


Fig. 8 Effect of dose rate, grafting temperature and Grafting time in grafting

△ 200 $\mu\text{W}/\text{cm}^2$, ○ 300 $\mu\text{W}/\text{cm}^2$,
× 400 $\mu\text{W}/\text{cm}^2$

vacuo. It is noted that both the tensile strength and the per cent elongation change scarcely after the irradiation times of about 10 min., but decrease steadily for longer irradiation times, and the decrease of the elongation was more rapid than that of the tensile strength. The irradiation time was 10 min. in the most of studies.

The effects of the dose rate, the grafting temperature and the grafting time are shown in Fig. 8. The per cent grafting increases with the grafting time. It soon arrives at a limiting value, respectively. The higher both the grafting temperature and the dose rate are, the higher the limiting value is. When the grafting temperature is elevated, the per cent grafting increases and then arises remarkably the swelling increase by polyacrylonitrile grafting and the crystallinity content decrease of polypropylene.

(2) Physical Properties of Grafted Films

Changing of Form — The grafted films become hard, expand and crease. The hardness increases with the per cent grafting and becomes remarkable when the per cent grafting is more than 30%. The hardness increases owing to the high glass point¹⁶⁾ of polyacrylonitrile. The grafted films become regularly thicker in all three dimensions. The per cent expansion is proportional to the per cent grafting.

Swelling in Dimethylsulfoxide and Carbontetrachloride— Polyacrylonitrile is dissolved easily in a solvent possessing the strong polarity as dimethylsulfoxide. On the other hand, the grafted film is insoluble, but swelled¹⁷⁾ in those solvents. The swelling did not occur at room temperature, but increased with the elevating of temperature and equilibrated in 40–50 min. The variation of the per cent swelling as a function of per cent grafting is shown in Fig. 9. where the swelling temperature was 110°C with dimethylsulfoxide and 75°C with carbontetrachloride, and the contact times was 4 hrs.

The swelling film does not adhere and possesses the property as well as gum. The swelling films were retained the initial dimension by removing the swelling agent. This fact indicates that the swelling agent is non solvent for the grafted polyacrylonitrile. Polypropylene film is dissolved in carbontetrachloride at 75°C. The grafted film does not swollen and the per cent

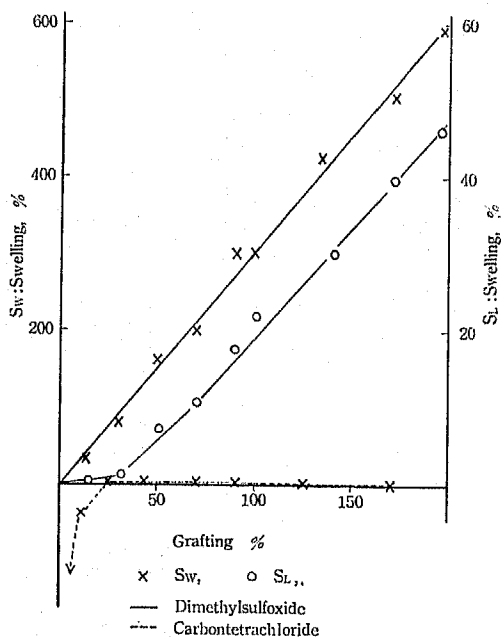


Fig. 9 Per cent swelling as a function of per cent grafting.

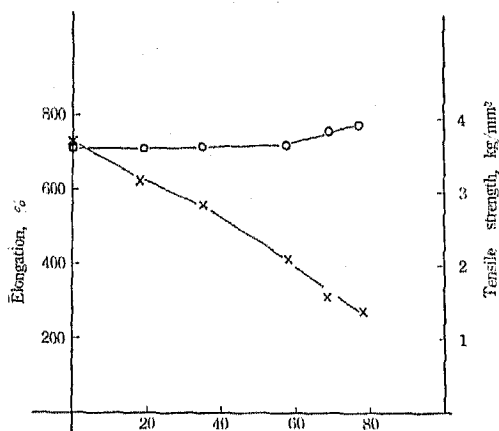


Fig. 10 Variation of tensile strength and elongation as a function of per cent grafting.

swelling (S_w) indicates rather the negative value by dissolving of polypropylene below 20% grafting.

Melting Point — For the ungrafted film, the melting occurred at 156°C, the material also flowed only slightly at 160°C. In the case of 30% grafting, the melting began at 160°C and ended at 180°C. For the film of 150% grafting, the material turn only from brown to black above 155°C. To determine the melting point as well as polyacrylonitrile film was difficult. The melting becomes slightly by grafting.

Tensile Strength and Per Cent Elongation — The measured values of tensile strength and per cent elongation are shown in Fig. 10.

Tensile strength increased slowly with the increase of per cent grafting, but per cent elongation decreased remarkably.

(3) Dyeability of Grafted Films

Dyeability — Results of the dyeing of the ungrafted films, various grafted films and polyacrylonitrile films are given in Table 3, 4, 5 and 6. The grafted films were dyed, but polypropylene and polyacrylonitrile films were not dyed. The degree of dyeing increases with the per cent grafting. More than 30%

Table 3 Dyeability of grafted films for basic dyes

Basic dyes	PP	Per Cent Grafting					PAN
		~15	15~25	25~35	35~45	45~	
Rhodamine G	-	+	++	###	###	###	-
Primoflauine	-	-	+	++	###	###	-
Diamond Green G	-	+	++	###	###	###	-
Magent Large Crystal	-	-	+	++	++	###	-
Methyl Violet Golden Star	-	-	++	###	###	###	-
Methylene Blue Conc	-	-	+	+	++	++	-
Crystal Violet 5BN	-	++	###	###	###	###	-
Mitsui Victoria Blue B Conc	-	++	###	###	###	###	-
Bismark Brown G Conc	-	+	++	###	###	###	-

PP : polypropylene film; PAN: polyacrylonitrile film; - undyeing;
+ light shades; ++ medium shades; ### dark shades.

Table 4 Dyeability of grafted film for Disperse dyes

Disperse dyes (Diacelliton)	PP	Per Cent Grafting					PAN
		~15	15~25	25~35	35~45	45~	
Red R Super Fine	-	+	++	###	###	###	-
Fast Pink B Super Fine	-	+	++	++	###	###	-
Fast Black D super Fine	-	+	++	###	###	###	-
Fast Yellow G Super Fine	-	+	+	###	###	###	-
Fast Green B Super Fine	-	+	++	###	###	###	-
Discharge Violet RG	-	+	++	###	###	###	-
Fast Navy Blue 5R Super Fine	-	+	++	++	++	###	-
Fast Dark Brown T Super Fine	-	+	++	###	###	###	-

Table 5 Dyeability of grafted film for Cationic dyes.

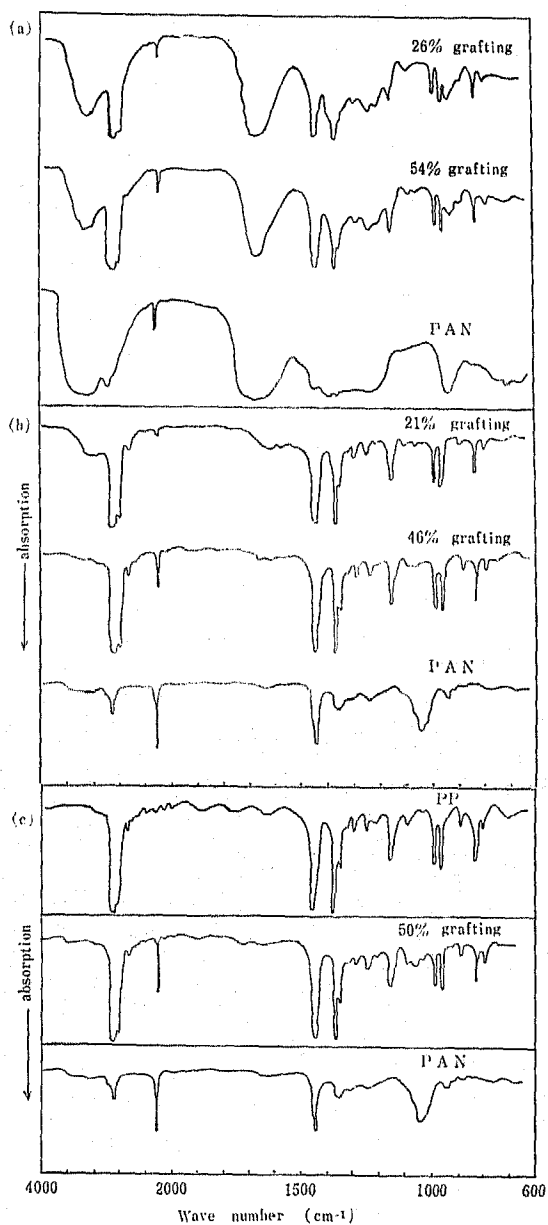
Cationic dyes (Astrazon)	PP	Per Cent Grafting					PAN
		~15	15~25	25~35	35~45	45~	
Red BBL	-	+	++	###	###	###	-
Red 5BL	-	+	++	++	++	++	-
Red F3BL	-	-	+	++	++	++	-
Yellow 7GLL	-	-	+	+	++	++	-
Yellow GLD	-	+	++	###	###	###	+
Yellow GL	-	-	+	+	++	++	-
Blue FGL	-	-	+	+	+	++	-
Blue BG	-	-	+	++	###	###	-
Blue 5GL	-	-	+	++	++	++	-

Table 6 Dyeability of Grafted film for Acid dyes

Acid dyes	PP	Per Cent Grafting				PAN
		~15	15~35	35~55	55~	
Acid Red R	(a)	-	++	-	-	-
	(b)	-	++	++	###	++
Acid Violet 5BN	(a)	-	###	-	-	-
	(b)	-	+	++	###	###
Orange II	(a)	-	++	-	-	-
	(b)	-	+	++	###	###

a grafted films treated with LiAlH_4 .

b grafted films treated with hydroxylamine HCl.



PP polypropylene film (ungrafted); PAN polyacrylonitrile film;
(a) Treating with Hydroxylamine.
(b) Treating with Lithium aluminium hydride.
(c) Control film.

Fig. 11 Infrared Spectra of aminated films and control films

grafted films were dyed in dark shades. It seems that the grafted polyacrylonitrile are not oriented to a high degree and are not tightly packed. It was found that the grafted film is dyed in the interior of the trunk polymer from the microscopical investigation of the section of film after dyeing. This fact indicated that the graft reaction occurs not only on the surface but also in the interior of the film.

In order to improve dyeability for acid dyes by amination, the grafted film was treated with reducing agents as hydroxylamine HCl and lithium aluminum hydride. In Fig. 11 is shown the infrared spectra of the grafted film, before and after amination by two different methods. Strongly absorbing ($-C=N$) band at 2215 cm^{-1} appear in grafted films. An examination of the infrared spectrum of the aminated films, except for polyacrylonitrile and the higher grafted films treating with lithium aluminum hydride, indicated the presence of (1710 cm^{-1} , $3100-3300\text{ cm}^{-1}$) bands which could be attributed to the amino group. The amination treated with lithium aluminum hydride was proved effective for 20-30% grafted films. The degree of dyeability of aminated films is shown in Table 7.

The degree of dyeability of these films is influenced by the degree of amination. Such aminated films can be dyed by acid dyes. Using 20-30% grafting of acrylonitrile it was possible to achieve improvements in dyeability without diminishing the excellent mechanical properties of the polypropylene.

Fastness to Light and Washing
— Fastness to light and washing was measured on dyeing films. The

results are listed in Table 8. From these data, it can be said generally that fastness to light is good to very good, washing fastness is low to good. In the cases of different grafted films dyed to equivalent deep shades with same dyes, the fastness to light of higher grafted films is superior to lower grafted films.

Table 7. Dyeability of grafted films dyeing with Red R Super Fine

Degree of grafting (%)	Dye absorbed $\times 10^{-4}$ mol	
	for grafted film (100g)	for grafted PAN (1mol)
0	trace	—
4	2.3	3.3
21	30.4	9.3
43	47.6	8.4
91	54.7	6.1

Table 8. Fastness of the Dyed Film to Light and Washing

Dye.		Fastness		
		Washing	Light	
Basic dyes	Rodamine G	+	+	*
	Diamond Green G	+	##	
	Methyl Violet Golden Star	++	++	
	Crystal Violet 5BN	+	##	
	Mitsui Victoria Blue B Conc	##	++	
	Bismark Brown G Conc	++	##	
Disperse dyes	Red R Super Fine	+	##	*
	Fast Black D Super Fine	+	++	
	Fast yellow G Super Fine	+	++	
	Fast Green B Super Fine	+	++	
	Discharge Violet RG	+	++	
	Fast Dark Brown T Super Fine	+	++	
Cationic dyes	Red BBL	++	++	
	Yellow GLD	+	++	
Acid dyes	Acid Red RS	++	++	
	Acid Violet 5BN	++	++	
	Orange II	++	++	

+ marked change; ++ moderate change; ## unchange.

* high grafted film.

(## change; |||| unchange for the irradiation time (10hr.))

Summary

This paper dealt with the grafting studies of acrylonitrile onto polypropylene films by ultraviolet preirradiation under vacuo and simultaneous irradiation in monomer vapour. That is to say, the effects of various factors, such as photosensitizer concentration, grafting time, grafting temperature, dose rate etc., were investigated, and the dyeability and physical properties of grafted films were also studied. The following results were obtained.

1. Regarding the photosensitizer, both benzophenone and anthraquinone were effective and the sensitizer concentration of 0.1-0.5%, w/w was useful for the grafting.

2. The per cent grafting increased with grafting time increase, but arrived soon at a limiting value. The higher both the grafting temperature and the dose rate were, the higher the limiting value was. When the grafting temperature was elevated, the per cent grafting increased and then the swelling property of the grafted films arose remarkably.

3. According to the results, the apparent activation energy of overall reaction was calculated to be 10.7 kcal. in this range 20-80°C.

4. The 30% and more grafted films were dyed in dark shades, but the original polypropylene films and pure polyacrylonitrile films were not dyed.

The grafted films could be improved the dyeability for acid dyes by amination. Using the 20-30% grafting of acrylonitrile, it was possible to achieve the improvements in dyeability of polypropylene films without diminishing the excellent mechanical properties.

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