

Graft Copolymerization of Hydrophilic Monomers onto Irradiated Polypropylene Fibers

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Synopsis

A method of graft copolymerization of hydrophilic monomers, such as 1-vinyl-2-pyrrolidone, acrylonitrile, acrylic acid, and acrylamide, onto irradiated polypropylene fibers has been studied. γ ray as well as electron beam were employed for the irradiation processes. Graft-copolymerization kinetics and the properties of grafted fibers have been investigated. Moisture regain, dyes absorption, and melting point of the grafted fibers were found to increase with the increasing of the degree of grafting. Polypropylene for 1-vinyl-2-pyrrolidone grafted fibers showed excellent dye absorption for almost all kinds of dyes such as direct, basic, acid, reactive, disperse, and naphthol dyes. However, for polypropylene acrylic acid grafted fibers, the colorfastness to washing was found to be unsatisfactory. The colorfastness to washing for polypropylene 1-vinyl-2-pyrrolidone grafted fibers was found to be fairly good for certain types of dyes such as vat and naphthol dyes.

INTRODUCTION

A hydrophobic synthetic fiber such as polypropylene (PP) fiber has drawbacks: the fiber is difficult to dye, has poor hygroscopicity, and is liable to accumulate electric charge. The method which comprises graft copolymerization, a hydrophilic monomer, onto such a fiber is a well known solution that overcomes the mentioned shortcomings. Acrylic acid or methacrylic acid are, for example, broadly used for that purpose. However, the use of acrylic acid or methacrylic acid has further drawbacks: that the resulting homopolymers frequently gel and their separation from the product to be obtained is difficult.

Investigations on radiation-induced graft copolymerization of hydrophilic monomers on PP fibers have been carried out in a number of countries. The properties of acrylic acid grafted fibers have been studied; they have high apparent melting points and high hydrophilicity has been detected. However, the sunlight aging was found to be unsatisfactory.^{1,2} Christin *et al.* have investigated the method of radiation grafting of methacrylic acid, vinyl 4-pyridine, and vinyl acetate monomers on PP fibers irradiated in the presence of air.³ Dyes absorption was found to be improved; however, this method of grafting was unsatisfactory because the resulting homopolymers were difficult to separate from the products. Investigations of the kinetics of graft copolymerization of gaseous vinyl chloride and vinylidene chloride on irradiated PP fibers found that the degree of grafting will increase directly proportional to the logarithm of reaction time.⁴

Radiation effect on polypropylene has been investigated by a number of investigators. Decker *et al.* have studied the degradation of polyolefin, atactic PP, by using γ irradiation in the presence of air. The formation of polypropylene hydroperoxide (POOH), dialkyl peroxide, and ketone have been detected.⁵ However, at a low dose rate of irradiation, the formation of POOH was more dominant than the other.

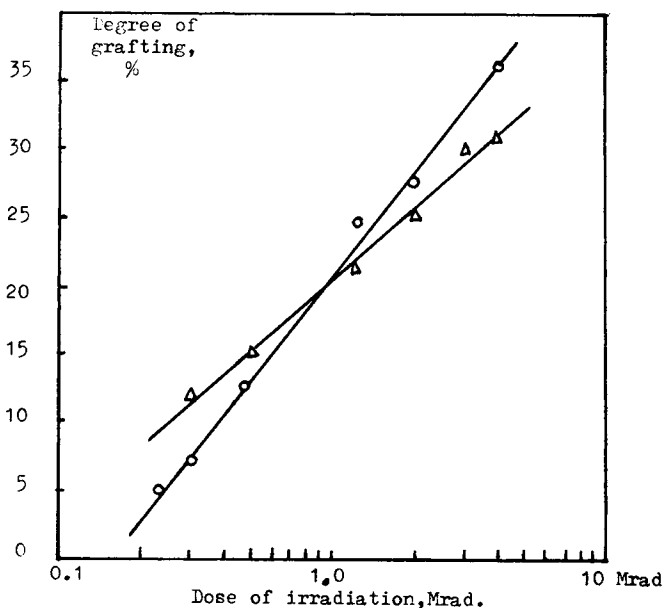


Fig. 1. Influence of irradiation dose on the degree of grafting of PP fibers. Reaction time 180 min at 60°C. O—O, 1-vinyl-2-pyrrolidone pure; Δ—Δ, solution of AA in water with AA concentration of 20%.

ESR studies on graft copolymerization of gaseous styrene onto irradiated PP concluded that the graft initiation activity was not at the trapped peroxy radicals but at the trapped carbon radicals.⁶ ESR studies of UV irradiation on PP indicated that methyl radicals, acyl radical, and alkyl radicals were found.⁷ The

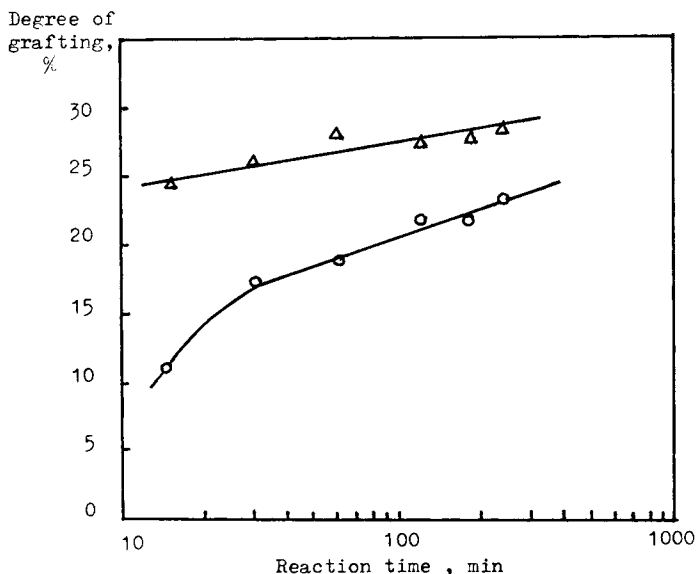


Fig. 2. Influence of reaction time on the degree of grafting of PP fibers. Reaction temperature 70°C and γ irradiation dose 1.357 Mrad. Δ—Δ, grafting with solution of AA monomer in water. Composition of solution: AA monomer 20% w/w, water 80%, w/w, and ferrousulfate 5 mg per 100 g of solution; O—O, grafting with VP monomer, pure.

effect of solvents on the graft copolymerization reaction by preirradiation techniques were investigated by Munari et al.⁸ Experimental results showed that the unusual interactions between the polymeric matrix and the monomer-solvent mixture are of greatest importance.

A method for modification of PP fibers by graft copolymerization with 1-phthalimido 1,3 butadiene by thermal mastication was studied by Terada.⁹ The filament can be dyed uniformly with some basic dyes at a rate proportional to the imidobutadiene contents.

The purpose of these experiments was to study the kinetics of graft-copolymerization reactions as well as to study the chemical and physical properties of grafted fibers. Hydrophilic monomers such as 1-vinyl-2-pyrrolidone (VP), acrylonitrile (AN), acrylic acid (AA), and acrylamide (AM) have been employed for these experiments. Graft copolymerization by preirradiation techniques was chosen for these experiments. It is well known that the amount of grafting is a function of radical concentration, monomer concentration, duration of polymerization, and temperature of polymerization.

THEORY

Reaction Kinetics of Peroxide Graft Copolymerization

In this method, the graft-copolymerization reaction is initiated by free radicals formed by thermal decomposition of dialkyl peroxide as well as by alkyl hydroperoxide decomposition. In the case of PP fibers, PP hydroperoxide can be formed by irradiation of PP fibers in the presence of air, presumably via a short chain process such as¹⁰

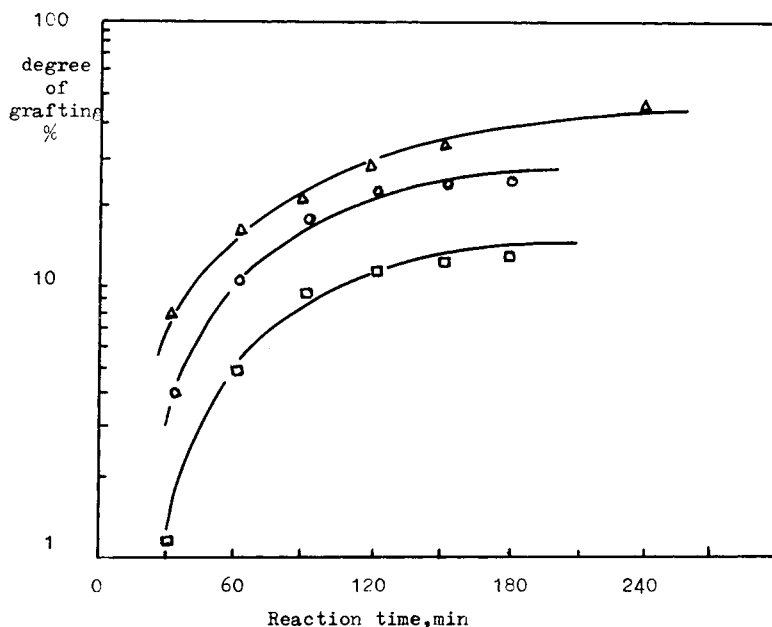


Fig. 3. Effect of reaction time on the degree of grafting of AN monomer on PP fibers. □—□, reaction temperature 50°C; ○—○, reaction temperature 60°C; △—△, reaction temperature 70°C.

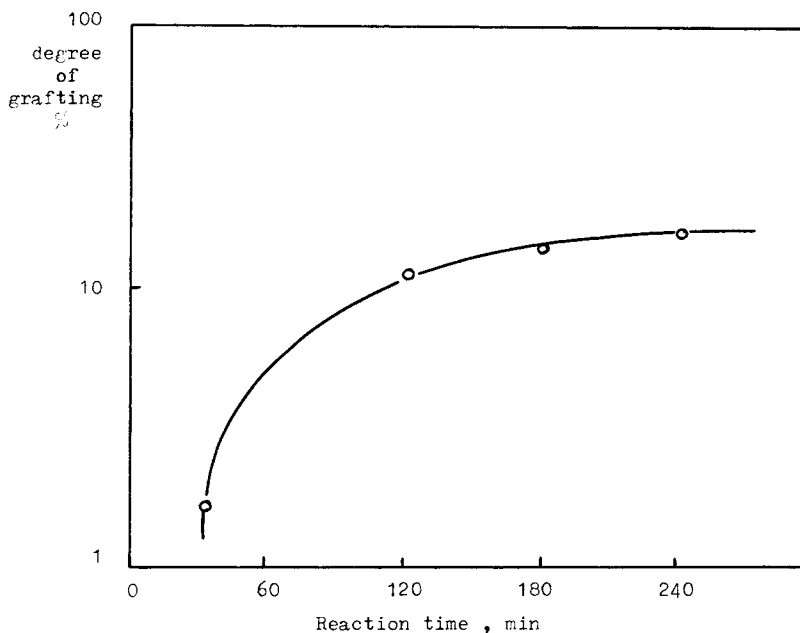


Fig. 4. Effect of reaction time on the degree of grafting of AM monomer on PP fibers. Monomer concentration 20 % w/w in water. γ irradiation in the presence of air. Reaction temperature 70°C.



According to Decker et al.,⁵ the principal product of PP (atactic) irradiation in the presence of air is polypropylene hydroperoxide (POOH); the other products are dialkyl peroxide, alcohol, and carbonyl compound. Thermal decomposition of POOH will produce $PO\cdot$ radicals and $OH\cdot$ radicals, where the kinetics scheme of that decomposition can be written



The rate of decomposition can be written

$$R_d = -d(POOH)/dt = k_d(POOH) \quad (5)$$

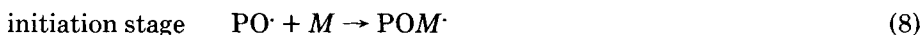
Integrating eq. (5) leads to

$$(POOH)_t = (POOH)_0 e^{-k_d t} \quad (6)$$

where $(POOH)_0$ is the concentration of polypropylene hydroperoxide for the decomposition duration t equal to 0; $(POOH)_t$ is the concentration of polypropylene for the decomposition duration equal to t ; and k_d is the rate constant of decomposition. Rearrangement of eqs. (5) and (6) leads to

$$R_d = k_d (POOH)_0 e^{-k_d t} \quad (7)$$

The radicals formed by thermal decomposition of POOH can initiate the graft-copolymerization reaction; the kinetic scheme of that reaction can be written



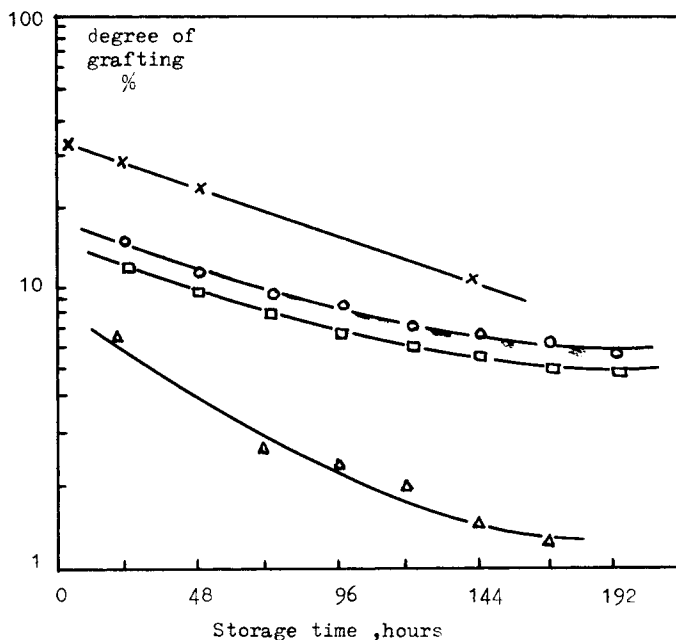
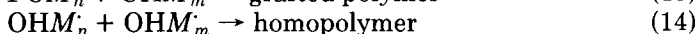
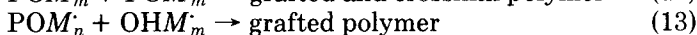
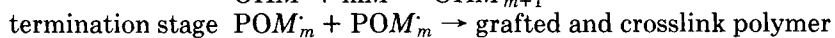


Fig. 5. Influence of storage time on the degree of grafting. $\Delta-\Delta$, PP fibers irradiated in the presence of air, γ irradiation with dose of irradiation 1 Mrad. Reaction grafting with a solution of AM monomer in water at 70°C for 2 hr. $\square-\square$, PP fibers irradiated in the presence of air, gamma, dose 1 Mrad. Grafting reaction with a solution of AM-An mixture in acetone at 70°C for 2 hr. $\circ-\circ$, PP fibers irradiated in the presence of air, gamma, dose of irradiation 1 Mrad. Grafting reaction with AN monomer at 70°C for 2 hr. $\times-\times$, PP fibers irradiated under vacuum, electron beam irradiation. Grafting reaction with a solution of AA monomer in water.



The rate of grafting R_g can be regarded as the rate of propagation in eq. (10) and be written

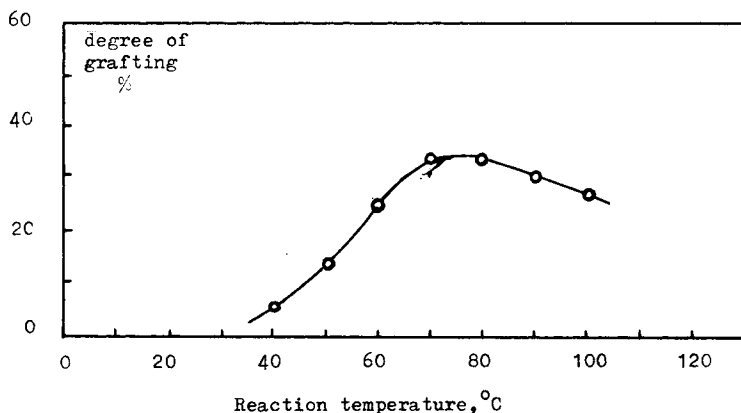


Fig. 6. Influence of reaction temperature on the degree of grafting of PP fibers. Grafting reaction with 1-vinyl-2-pyrrolidone monomer in pure condition. Dose of γ irradiation 1.92 Mrad.

TABLE I
Melting Point and Moisture Regain of Grafted Fibers

Grafted fibers	Degree of grafting, %	Melting point, °C	Moisture regain, % at relative humidity 65%
PPVP ^a	12.0	230	1.50
	13.9	233	2.10
	16.8	>300	2.50
	27.8	>300	4.20
PPAN ^b	1.4	164.1	0.20
	6.9	193.7	0.43
	10.4	197.4	0.32
	14.1	211.7	0.33
	25.8	217.6	0.26
PPAM ^c	1.2	162.7	3.17
	2.6	163.7	3.01
	3.6	165.6	2.47
	7.1	167.0	1.99
PPAA ^d	13.4	169.3	2.60
	12.1	223.0	0.70
	18.8	>300.00	1.60
	25.5	>300.0	2.50
PPANa ^e	8.0	180.0	...
	13.6	258.0	1.90
	18.6	>300.0	1.90
	22.5	>300.0	4.00
	24.5	>300.0	3.10
PP	0.0	163.0	0.00

^a PP fibers grafted with VP monomer.

^b PP fibers grafted with AN monomer.

^c PP fibers grafted with AM monomer.

^d PP fibers grafted with AA monomer.

^e PP fibers grafted with ANa monomer.

$$R_g = k_p(\text{POM}\cdot)(M) \quad (15)$$

where $\text{POM}\cdot$ is the concentration of peroxide radicals at all stages; the mathematical formula can be written $(\text{POM}\cdot) = \sum_1^n (\text{POM}\cdot_n)$.

At a steady state it can be assumed that the rate of termination is equal to the rate of radical production or the rate of polypropylene hydroperoxide decomposition and can be written

$$k_d(\text{POOH})_0 e^{-k_d t} = k_{t'}(\text{POM}\cdot)^2 + k_{t''}(\text{POM}\cdot)(\text{OHM}\cdot) + k_{t'''}(\text{OHM}\cdot)^2 \quad (16)$$

Assuming that the concentration of $\text{OHM}\cdot$ radicals equals the $\text{POM}\cdot$ radicals, a more simplified equation can be written

$$k_d(\text{POOH})_0 e^{-k_d t} = k_t(\text{POM}\cdot)^2 \quad (17)$$

Rearrangement of eqs. (15) and (17) leads to

$$R_g = dG/dt = k_p(M)(k_d)^{1/2}(\text{POOH})_0^{1/2}(k_t)^{-1/2}e^{-k_d t/2} \quad (18)$$

For the simplification of that equation, it is postulated that the concentration of the monomer (M) in the reaction site does not change widely with time, except at the beginning of the reaction and as for termination constant k_t . Integrating eq. (18) leads to

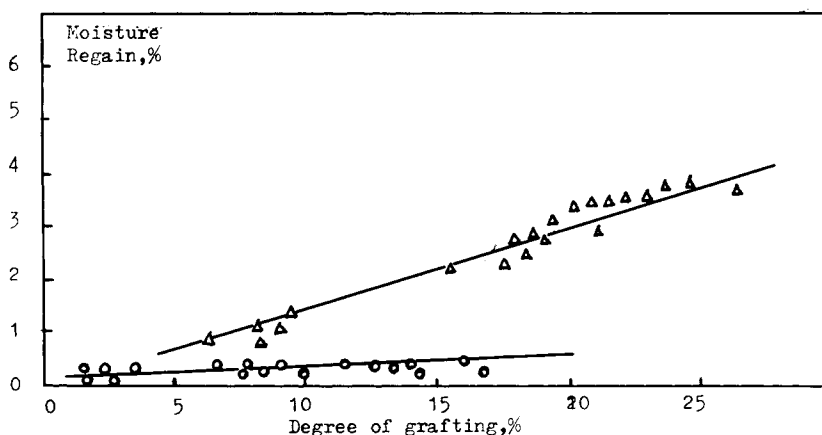


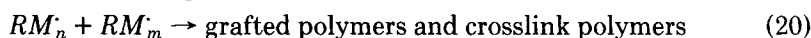
Fig. 7. Influence of the degree of grafting on the moisture regain of PP grafted fibers, measured at 65% of relative humidity and 25°C. Δ — Δ , PPVP; \circ — \circ , PPAN.

$$G = 2k_p(\text{POOH})_0^{1/2} (M)(k_t k_d)^{-1/2} (1 - e^{-k_d t/2}) \quad (19)$$

This equation shows that the degree of grafting should be directly proportional to M and to the square root of $(\text{POOH})_0$. At low dose of irradiation, the concentration of polypropylene hydroperoxide $(\text{POOH})_0$ is directly proportional to the dose of irradiation.

Reaction Kinetics of Trapped Radical Graft Copolymerization

In this method, the graft-copolymerization reaction is initiated by trapped radicals which were usually formed by irradiation of polymeric materials in the absence of air. The number of radicals, trapped radicals, and growing chains will decrease with time owing to chain termination and radical recombination according to the following reaction:



The rate of termination can be written

$$R_t = -d(RM\cdot)/dt = k_t(RM\cdot)^2 \quad (21)$$

TABLE II
Grafting of 1-Vinyl-2-Pyrrolidone Monomer on PP Fibers Initiated by Trapped Radicals.
Irradiation under Electron Beam at 20°C. Grafting Temperature 60°C

Irradiation dose, Mrad	Reaction time, min	Monomer concentration in water, %	Degree of grafting, %	Moisture regain, %
0.99	60	10	3.86	0.36
0.99	120	10	6.37	0.63
0.99	180	10	6.42	0.62
0.99	60	50	9.30	1.30
0.99	120	50	11.30	1.50
0.99	180	50	10.10	1.40
0.99	30	75	12.00	1.50
0.99	60	75	13.90	2.10
0.99	120	75	16.80	2.50
1.98	30	75	27.80	4.20
1.98	60	75	27.90	4.00
1.98	120	75	27.00	5.30

TABLE III
 Dyes Absorption for Grafted Fibers

	Dye	PP	PPAA	PPVP	PPAN	PPAM
Vat dyes:	1. Indathrene brilliant Rose	C ^a	A	A	C	C
	2. M.N.Thren Grey	C	C	A	C	C
	3. M.N.Thren Olivet	C	A	A	C	C
	4. Indigoso Red IFBB	C	B	A	C	C
Acid dye:	1. Neonyl Orange	C	A	A	C	C
	2. Neonyl Red 2 B	B	A	A	C	C
	3. Neonyl Golden Yellow	C	B	A	C	C
Basic dye:	1. Astra Neofuchsin	B	A	A	C	A
	2. Malachite Green	C	A	A	C	A
	3. Rhodamine B	B	A	A	C	A
	4. Marine Blue	C	A	A	C	A
	5. Methyl Violet	C	A	A	C	A
Direct dye:	1. Durazol Orange RS	C	B	A	C	A
	2. Durazol Brown R300	C	B	A	C	—
	3. Durazol Yellow 4G5	C	A	A	C	—
Dispers:	1. Palanil Red 5BEL	B	A	A	A	—
	2. Palanil Yellow R	C	A	A	A	—
	3. Palanil Blue RT	B	A	A	A	—
	4. Red Violet FR	B	A	A	A	A
Reactive:	1. Procion Yellow MR	B	B	A	C	C
	2. Procion Black MB	C	C	A	C	C
Naphthol as +:	1. α naphthylamine	B	A	A	B	A
	2. β naphthylamine	B	A	A	B	A
	3. β nitroaniline	B	A	A	B	A

^a A = deeply colored, B = faintly colored, C = does not absorb dyes at all.

where (RM^\cdot) is the concentration of all growing radicals at all stages, including macro and small radicals that exist in the polymer matrix. A mathematical formula can be written

$$(RM^\cdot) = \sum_1^n (RM_n^\cdot) \quad (22)$$

Integration of eq. (21) leads to

$$(RM^\cdot) = (RM^\cdot)_0 [1 + k_t (RM^\cdot)_0 t]^{-1} \quad (23)$$

where $(RM^\cdot)_0$ is the concentration of trapped radicals for the duration of reaction t equal to zero. The rate of grafting can be written

$$R_g = dG/dt = k_p(M)(RM^\cdot) \quad (24)$$

It can be assumed that at steady state, the monomer concentration at the reaction site M is constant during the reaction owing to the rapid supply of monomers. Then from the above assumption eqs. (24) and (23) can be integrated leading to

$$G = k_p k_t^{-1}(M) \ln[1 + k_t (RM^\cdot)_0 t] \quad (25)$$

This equation is a general equation for the degree of grafting initiated by trapped radicals. At a sufficiently large value of t , eq. (25) can be simplified

$$G = k_p k_t^{-1}(M) \ln\{k_t (RM^\cdot)_0 t\} \quad (26)$$

This equation shows that the degree of grafting should be directly proportional to M and to the logarithm of reaction time t and trapped radical concentration. In the case of a low dose of irradiation, it can be assumed that the concentration of trapped radicals should be directly proportional to the dose of irradiation. Then the degree of grafting should be proportional to the logarithm of irradiation dose while the other parameter is constant.

EXPERIMENTAL

Materials

Polypropylenes employed in these experiments were in the fibrous form, supplied by Phillips Company. The diameter of this fiber was about 0.01 mm and the fraction soluble in toluene was about 12.5%. Samples of polypropylene (PP) fibers were purified by washing in a solution of detergent, dried, and stored in a desiccator over silica gel or calcium chloride.

Hydrophilic monomers such as VP, AA, AN, and AM were supplied by Merck Company. Monomers such as VP, AA, and AN were purified by vacuum distillation at low temperature and then the purified products stored at low temperature. In the case of the AM monomer, purification by recrystallization was employed.

Radiation Sources

γ radiation source of Co-60, gammacell 220, with irradiation dose rate of about 2.8×10^5 rad/hr was employed in these experiments. This radiation source is located at Pasar Jumat Atomic Energy Research Center, Indonesia. Another radiation source, Van de Graff electron accelerator, Vulcain, 3 MeV and 1 mA, was also employed for these experiments. This radiation source is located at CEN de Saclay, French.

TABLE IV
Colorfastness to Washing for PPAA Fibers at 40°C

Dye	Geometric grey scale		Effect on the pattern
	Degree of staining against cotton fibers	Degree of staining against PPAA fibers	
<u>Acid dye</u>			
1. Nylomine Yellow C-8G	4	4	2-3
2. Nylomine Brown C-R	2	2	1-2
3. Nylomine Blue C-R	2	1-2	1-2
<u>Basic dye</u>			
1. Astra Neofuchsin Crystal	3	4	3
2. Marine Blue	3	4	3
3. Astra Diamond Green	4-5	4	4
<u>Direct dye</u>			
1. Solophenyl Red 6 BL	4	4	3-4
2. Solophenyl Yellow FFL	3	1-2	1
3. Solophenyl Brilliant Blue BL	3	3	3-4

TABLE V
Colorfastness to Washing for PPVP Fibers at 40°C

Dye	Geometric grey scale	
	Degree of staining against polyester fibers	Effect on the pattern
Naphthol dye		
1. Naphthol AS + α naphthylamine	3	2
2. Naphthol AS + β nitroaniline	3	3
3. Naphthol AS + β naphthylamine	3	3
Reactive dye		
1. Procion Yellow MR	4	1
2. Procion Black MB	2	1
Dispers dye		
1. Red Violet	3	1
2. Palanile Yellow R	3	1
3. Palanile Blue RT	2	2
Direct dye		
1. Durazol Orange RS	1	3
2. Durazol Brown R300	2	3
3. Durazol Yellow 4 G 5	1	2
Vat dye		
1. Indanthren Brilliant Rose	3	3
2. M.N. Thren Grey M	3	3

Irradiation

Irradiation process was carried out either by gamma or electron beam. In the case of AA or VP graft copolymerization, the trapped radicals graft-copolymerization method was employed. In this method a sample of PP fibers of about 3000 mg weight, was put into a glass tube fitted with ground joint, evacuated to 1.75×10^{-2} Torr, and irradiated at room temperature. In the case of electron-beam irradiation, the irradiation dose was measured with tricellulose acetate dosimeter,¹¹ and with Fricke dosimeter in the case of γ irradiation.

In the case of AN and AM monomers, the peroxide graft-copolymerization method was employed in these experiments. In this method a sample of PP fibers of about 3000 mg weight was irradiated in the presence of air at room tem-

TABLE VI
Colorfastness to Washing for PPAN Fibers at 40°C

Dye	Geometric grey scale		
	Degree of staining against Polyester	Cotton	Effect on the pattern
Dispers			
1. Palanil Yellow R	4	4	3-4
2. Palanil Red 5 BEL	4	4	3-4
3. Palanil dark Blue 3RT	4	4	3-4
Naphthol			
1. Naphthol AS BO + β naphthylamine	2	4	4
2. Naphthol AS BO + G.N. Fast Red	3	4	2-3
3. β naphthol + G.N. Fast Red	3	4	2-3
4. β naphthol + β naphthylamine	2	4	3

perature; polypropylene hydroperoxide will be formed in this irradiation method.

Grafting Reaction

Grafting reactions were carried out in a vacuum glass tube placed in controlled temperature waterbath or oilbath. The irradiated sample, still in the vacuum tubes, was filled with the mentioned monomer solution and placed in that temperature controlled waterbath. The reaction temperature was between 40 and 100°C and the reaction time was between 15 and 240 min. After the grafting reactions were completed, the samples were washed several times with hot water for removal any homopolymer which may be present in the products and finally dried in an oven until a constant in weight. Ferrosulfate or cupriacetate solution was employed for inhibiting the formation of the homopolymer.^{12,13}

The apparent degree of grafting can be calculated as follows: $G = (W - W_0)/W_0 \times 100$, where G is the apparent degree of grafting expressed in %, W is the weight of the sample after grafting, and W_0 is the weight of the sample before grafting.

Physical and Chemical Testing

Physical and chemical properties of grafted fibers such as moisture regain, melting point, dyes absorption, and color fastness were determined according to the procedure in Indonesian Standard of Textile Testing.¹⁴

RESULTS AND DISCUSSION

Influence of Irradiation Dose

The variation of the degree of grafting with irradiation dose is illustrated in Figure 1. In this figure it can be seen that the degree of grafting appeared to increase directly proportional to the logarithm of the irradiation dose. These obtained results appeared to be in agreement with the graft-copolymerization kinetics initiated by trapped radicals. For a low dose of irradiation it can be assumed that the concentration of trapped radicals is proportional to the dose of irradiation. Based on this assumption and on the kinetics of trapped radicals initiation, it could be concluded that the degree of grafting should be directly proportional to the logarithm of the irradiation dose.

Influence of Reaction Time

Irradiation in the Absence of Air

In these experiments, samples of PP fibers with a weight of about 3000 mg of each sample, are γ irradiated under vacuum condition. Solution of the AA monomer in water as well as the pure VP monomer was employed for the grafting reaction. The variation of the degree of grafting with the reaction time is illustrated in Figure 2. The reaction temperature and irradiation dose employed for these experiments are indicated in this figure. It is seen that the degree of grafting increases directly proportional to the logarithm of the reaction time,

which apparently is in agreement with the graft-copolymerization kinetics initiated by trapped radicals. However, for a short reaction time (may be under 15 min) the steady state of the grafting reaction apparently is unreachd; then, in this region, the curve is not a straight line, and the degree of grafting is lower than expected.

Irradiation in the Presence of Air

In these experiments, samples of PP fibers were irradiated in the presence of air at room temperature by γ irradiation. A monomer of AN was employed for the grafting reaction. The temperatures of the grafting reaction were 50, 60, and 70°C, respectively. Variation of the degree of grafting with reaction time is illustrated in Figures 3 and 4. It can be seen that the degree of grafting increases with the reaction time, reaching maximum level after 2–3 hr of reaction time. In these experiments many homopolymers were formed; however, these homopolymers can be easily separated from the products.

It can be seen that the maximum degree of grafting increases with the reaction temperature. Theoretical studies on the kinetic scheme of peroxide graft copolymerization concluded that the maximum degree of grafting can be written

$$G = 2k_p(\text{POOH})_0^{1/2} (M)(k_d k_t)^{-1/2}$$

According to Arrhenius, the value of the rate constant is dependent on reaction temperature and activation energy. The maximum degree of grafting can then be written

$$G_m = 2A_p(\text{POOH})_0^{1/2} (M)(A_t A_d)^{-1/2} e^{-\Delta E/RT}$$

where ΔE is the overall activation energy. It can also be seen that the maximum degree of grafting at 50°C is about 18%, at 60°C is about 27%, and at 70°C is about 42%. From the above results, the overall activation energy was calculated and found to be 8.9 kcal/mole.

Influence of Storage Time

In these experiments, samples of PP fibers were γ or electron-beam irradiated. These irradiated samples were stored at room temperature for several days. After a certain storage time, the irradiated samples were grafted with a solution of monomer. Variation of the degree of grafting with storage time is illustrated in Figure 5. It is seen that the degree of grafting decreases with the storage time and must be due to the decreasing of peroxide concentration or trapped radical concentration. Concentration of polypropylene hydroperoxide at any storage time can be written

$$(\text{POOH})_t = (\text{POOH})_0 e^{-k_d t}$$

From the above equation it can be concluded that the logarithm of the degree of grafting must decrease directly proportional to the storage time. However, this statement is true when the value of k_d is constant during the storage time. In practice, this value decreases with time because the more decomposable peroxide will decompose first, while the most stable radicals decompose later and have a lower decomposition constant k_d .

The decomposition constant k_d decreases with time. The results illustrated in Figure 5 apparently are in agreement with this statement, namely, the slope of the curve appeared to decrease with the storage time.

In the case of the trapped radical graft-copolymerization method, the trapped radical concentration at any time can be written

$$(R\cdot)_t = (R\cdot)_0[k_t(R\cdot)_0t + 1]^{-1}$$

where $(R\cdot)_t$ is the concentration of the trapped radicals at a storage time equal to t , and $(R\cdot)_0$ is the concentration of trapped radicals at the beginning. From the above equation it can be calculated that the degree of grafting would decrease directly proportional to the logarithm of the storage time.

Influence of Reaction Temperature

With the increase of the reaction temperature, the rate of grafting could be expected to increase. However, the rate of radical recombination also increases with the increase of reaction temperature, resulting in the decreasing rate of grafting. Influence of reaction temperature on the degree of grafting is illustrated in Figure 6. It is seen that the degree of grafting increases with the reaction temperature until a maximum value is reached at temperature of about 70°C and then it decreases with reaction temperature.

Melting Point and Moisture Regain

The melting point and moisture regain of PP grafted fibers were determined according to the general procedure of ISTT.¹⁴ The results of these determinations are tabulated in Table I. The increase of melting point and moisture regain with the degree of grafting were found in all PP grafted fibers. VP and AA monomers have proved to be the most excellent monomers for improvement of either melting point or moisture regain of PP fibers. PP grafted fibers with a melting point higher than 300°C have been produced. The influence of degree of grafting on moisture regain is illustrated in Figure 7. Moisture regain of PPVP fibers increases with the increase of degree of grafting.

Dye Absorption

Samples of grafted fibers were used for these dyeing experiments; almost all kinds of dyes were employed, which included direct, naphthol, dispers, reactive, basic, acid, and vat dyes. The results of these experiments are tabulated in Table III, IV, V, and VI. In Table III it can be seen that PPVP fibers absorb almost all kinds of dyes. However, PPAA fibers only absorb a certain kind of dye such as basic, acid, dispers, and naphthol dyes. PAN fibers only absorb dispers dye and limited amounts of naphthol dyes. It appeared that hydrophilic fibers will absorb dyes better than hydrophobic fibers. However, washing colorfastness for PPAA fibers was found to be poor except for basic dyes (Table IV). Washing colorfastness for PPVP fibers was found to be fairly good for a certain kind of dye such as vat and naphthol dyes (Table V). In Table VI it can be seen that washing colorfastness for PAN fibers colored with dispers and naphthol dyes appeared to be fairly good. The degree of staining for these colored fibers was found to be above a value of 3, as compared with a value of 5 for perfectly unstained colored fibers.

CONCLUSION

Polypropylene grafted fibers can be produced easily by using irradiation technique. Hydrophilic monomers grafted onto irradiated polypropylene fibers yield fibers of higher moisture regain, higher melting point, and better dye absorption. Washing colorfastness for polypropylene grafted fibers was found to be dependent on the type of dyes and monomers selected for the grafting reaction.

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References

1. W. Tsuji, T. Ikeda, M. Hamanaka, and Y. Ikeda, *Bull. Inst. Chem. Res. Kyoto Univ.*, **45**(1) (1967).
2. W. Tsuji, T. Ikeda, M. Hamanaka, and Y. Ikeda, *Int. Fiber Conf.*, Dornbin, Austria, 1971.
3. D. Christin and J. Degret, *Amelioration de l'affinite tinctorial du polypropylene par voie radiochimique*, Ensait, France, 1966.
4. K. Hayakawa and K. Kawase, *J. Polym. Sci., Part A-1*, **5**, 439 (1967).
5. C. Decker and F. R. Mayo, *J. Polym. Sci.*, **11**, 2847 (1975).
6. Y. Hama, T. Ooi, M. Shiotsubo, and Shinohara, *Polymer*, **15**, 787 (1974).
7. K. Nunone, B. Eda, and M. Iwasaki, *J. Appl. Polym. Sci.*, **18**, 2711 (1974).
8. S. Munari, G. Tealdo, F. Vigo, and C. Rossi, *Eur. Polym. J.*, **4**, 241 (1968).
9. A. Terada, *J. Appl. Polym. Sci.*, **12**, 35 (1968).
10. A. Chapiro, *Radiation Chemistry of Polymeric System*, Wiley, New York, 1962, p. 444.
11. J. R. Puig, J. Laizier, and F. Sundardi, *Symposium on Radiosterilization of Medical Products*, IAEA, Vienna, 1975.
12. J. C. Bonnefis and J. R. Puig, *J. Appl. Polym. Sci.*, **15**, 553 (1971).
13. M. B. Huglin, B. L. Johnson, and R. W. Richards, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1363 (1976).
14. DSTI 1971-1972-1973, Indonesian Standard of Textile Testing.

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