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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Kawai, Wasaburo and Ichihashi, Taichi(1974) 'Photoinduced Graft Copolymerization of Acrylic Acid-n-Butyl Acrylate on Polyvinyl Chloride', *Journal of Macromolecular Science, Part A*, 8: 4, 805 – 818

To link to this Article: DOI: 10.1080/00222337408066399

URL: <http://dx.doi.org/10.1080/00222337408066399>

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Photoinduced Graft Copolymerization of Acrylic Acid—n-Butyl Acrylate on Polyvinyl Chloride

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ABSTRACT

The photoinduced graft polymerization of acrylic acid and n-butyl acrylate on polyvinyl chloride or carbon monoxide-vinyl chloride copolymer by using benzophenone as a sensitizer was carried out. In graft polymerization of acrylic acid, the degree of grafting was low. However, graft polymerization of n-butyl acrylate or acrylic acid—n-butyl acrylate were higher than that of acrylic acid. Turbidimetry, DTA, and TGA of the graft polymer were examined. As the graft polymer was a weak polyacid, the pK_a was estimated according to the Henderson equation, and the relationship between pK_a and the acrylic acid unit content in the graft polymer was derived.

INTRODUCTION

In order to bind a hydrophilic group on polyvinyl chloride (PVC), photoinduced graft polymerization on the polymer was studied. Smets [1] reviewed graft polymerization extensively. Graft polymerization

by chain transfer on PVC has been reported by several authors [2-5]. Photoinduced graft polymerization on cellulose, natural rubber latex, and polyethylene has also been reported by many authors [6-12], and graft polymerization by photolysis was reported by Guillet [13]. Recently, graft polymerization of acrylic acid on polyethylene and polypropylene has been carried out by peroxide, redox, and γ -ray methods [14-16].

In the present study it was found that graft polymerization of acrylic acid or alkyl acrylate on PVC in an appropriate quantity of solvent (tetrahydrofuran, cyclohexanone, and dioxane) proceeded by photoirradiation with benzophenone as a sensitizer. Acrylic acid showed a low degree of grafting for polyvinyl chloride due to phase separation, but alkyl acrylates such as n-butyl acrylate, which have a compatibility for PVC, brought favorable results. Thus, graft polymerization of acrylic acid and n-butyl acrylate on PVC occurred with good results. On the other hand, photoinduced graft copolymerization of acrylic acid and n-butyl acrylate on carbon monoxide-vinyl chloride copolymer was carried out in cyclohexanone and dioxane, but only in dioxane was the graft polymer formed.

EXPERIMENTAL

Materials

Polyvinyl chloride was prepared according to the procedure described in the previous paper [17]. Carbon monoxide-vinyl chloride copolymer was prepared by emulsion copolymerization [18]. Acrylic acid, n-butyl acrylate, and solvents were used after distillation of commercial grade.

Procedure of Photografting

A flask equipped with a high-pressure mercury lamp (100 W) at the center and a side tube for air evacuation was used as the apparatus for photoirradiation. Polymer, solvent, and monomer were charged into the flask and left overnight. The polymer was dissolved and partially highly swollen. Then the photosensitizer, benzophenone, was charged and stirred thoroughly. After air evacuation, the flask was immersed in a thermostat bath at 80°C and irradiated immediately under a nitrogen stream. After photoirradiation the polymerization product was poured into a large quantity of n-hexane, and then the collected polymer was refluxed in benzene for extraction. In addition, thorough extraction with methanol was carried out. The residual polymer was dried at 60°C in a vacuum oven. The degree of grafting and graft efficiency were estimated by

$$\text{degree of grafting} = \frac{\text{wt increase}}{\text{wt of original polymer}} \times 100(\%)$$

$$\text{graft efficiency} = \frac{\text{wt of grafting monomer}}{\text{wt of consumed monomer}} \times 100(\%)$$

Estimation of Carboxyl Group and Turbidimetry of Graft Polymer

The graft polymer was dissolved in tetrahydrofuran and titrated with 0.01 N sodium hydroxide aq solution using a autotitrating apparatus (Hirama Rika Kenkyujo, Kawasaki, Japan). Turbidimetry of the graft polymer in tetrahydrofuran was carried out by the titration of water with the same apparatus at 655 m μ .

DTA and TGA of Graft Polymer

DTA and TGA of the graft polymer and the original polymer were measured between 20 and 650°C with at a rate of 10°C/min under nitrogen stream.

RESULTS AND DISCUSSION

The results of the graft polymerization of acrylic acid on PVC are shown in Table 1. The weight increase after photoirradiation was high, but the degree of grafting was very low because most of the polyacrylic acid was extracted with methanol as ungrafting homopolymer. In spite of the low degree of grafting, the IR spectrum of the polymer shows the absorption of the carboxyl group at 1710 cm⁻¹ as indicated in Fig. 1.

The results of the graft polymerization of n-butyl acrylate on PVC are shown in Table 2. Graft polymerization without solvent gave a low degree of grafting, but that in solvent gave an increased degree of grafting. The graft polymer was reprecipitated with methanol from tetrahydrofuran solution for purification. The IR spectrum of the polymer is shown in Fig. 2, and the sharp absorption of ester carbonyl group is observed at 1730 and 1165 cm⁻¹. The result of the graft polymerization of acrylic acid and n-butyl acrylate on PVC is shown in Table 3. After extraction with benzene and methanol, the residual polymer was obtained as the graft polymer. The IR spectrum of the graft polymer is shown in Fig. 2, and the absorption of the ester carbonyl group is recognized at 1165 and 1730 cm⁻¹ with that of the

TABLE 1. Graft Polymerization of Acrylic Acid on PVC

No.	Polymer (g)	Solvent (cc)	Acrylic acid (cc)	Benzophenone ^a (g)	Temp (°C)	Irradiation time (min)	ΔWt^b
1	0.325	THF (5)	0.5	0.013	60	105	0.28
2	0.361	THF (5)	2	0.033	60	90	1.34
3	0.332	THF (5)	0.5	0.012 ^c	60	100	~0
4	-	THF (5)	0.5	0.012	60	100	0.33
5	0.368	CY (5)	2.0	0.038	100	30	1.70
6	0.351	CY (5)	2.0	0.031	80	30	1.78
7	0.347	DIO (5)	2.0	0.031	80	120	1.63
8	-	CY (5)	2.0	0.031 ^d	100	30	0.35

^aExcept for No. 3.

^b ΔWt indicates weight increase after polymerization.

^cBenzoyl peroxide (0.012 g) was used without photoirradiation.

^dNo photoirradiation was made.

TABLE 2. Graft Polymerization of n-Butyl Acrylate on PVC

No.	Polymer (g)	Solvent (cc)	n-Butyl acrylate (cc)	Benzophenone (g)	Temp (°C)	Irradiation time (min)	Degree of grafting (%)	Graft Efficiency (%)
1	0.850	-	6	0.037	90	180	4.9	-
2	0.770	-	6.4	0.025 ^a	"	40	18.1	-
3	0.370	THF (5)	2	0.033	60	90	10.5	7.2
4	0.945	THF (4)	7	0.030	60	140	24.9	4.2
5	0.990	CY (2)	7	0.038	80	180	87.0	15.1
6	1.007	DIO (2)	7	0.031	80	180	21.3	-

^a Benzoyl peroxide (0.025 g) was used without photoirradiation.

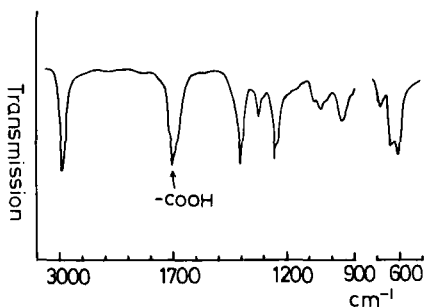


FIG. 1. Infrared spectrum of graft polymer of acrylic acid on PVC.

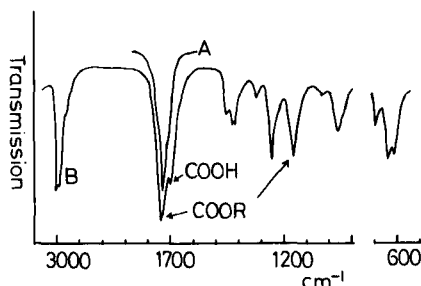


FIG. 2. Infrared spectrum of graft polymer of n-butyl acrylate (A) and n-butyl acrylate-acrylic acid (B) on PVC.

carboxylic group at 1710 cm^{-1} as a shoulder band of 1730 cm^{-1} . The degree of grafting and graft efficiency increased with the total monomer concentration (BA/AA = about 5, mole ratio) as shown in Fig. 3.

The turbidimetric differences between the graft polymer and the mixed polymer on PVC are shown in Fig. 4. In the graft polymer solution, turbidity was higher than in the mixed polymer solution with an increase of titrant (water). In PVC solution, turbidity occurred at an earlier stage, and a decrease of turbidity due to phase separation was recognized at a later stage. Thermal analysis of the graft polymer was carried out by TGA and DTA as shown in Fig. 5. Thermal stability of graft polymer at 260 to 400°C was superior to that of PVC. The two endothermic peaks of the graft polymer are observed at 290 and 305°C . However, these peaks were not observed in PVC which was prepared at room temperature by organoaluminum- $\text{CuCl}-\text{CCl}_4$ catalyst, although in commercial PVC (for example, Zeon Resin 121), a sharp peak is distinctly observed at 290°C .

TABLE 3. Graft Copolymerization of n-Butyl Acrylate—Acrylic Acid on PVC^a

No.	Polymer (g)	Solvent (cc)	n-Butyl acrylate			Acrylic acid			Degree of grafting (%) ^b	Grafting efficiency (%)
			cc	mole	cc	mole	cc	mole		
1	1.109	CY (6)	7	0.0528	1.5	0.0220	1.52	136.7	41.4	
2	1.00	CY (10)	6	0.0453	1.2	0.0175	0.50	49.7	14.9	
3	1.037	CY (12)	3	0.0226	0.5	0.0073	0.31	29.9	19.7	
4	1.026	CY (12)	3	0.0226	0.5	0.0073	0.18	17.1	-	
5	1.052	CY (10)	4	0.0302	0.65	0.0095	0.44	41.9	20.4	

^aGraft copolymerization was carried out at 80°C for 2.5 hr with 0.035 g of benzophenone.

^b Δ Wt indicates weight increase after extraction of polymerization product with benzene and methanol.

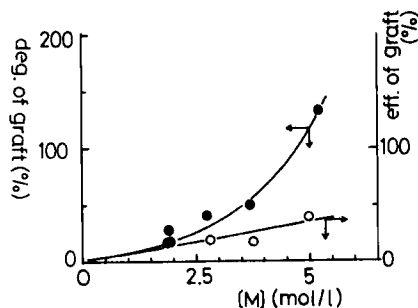


FIG. 3. Dependence of degree of grafting and graft efficiency on monomer concentration (n-butyl acrylate and acrylic acid).

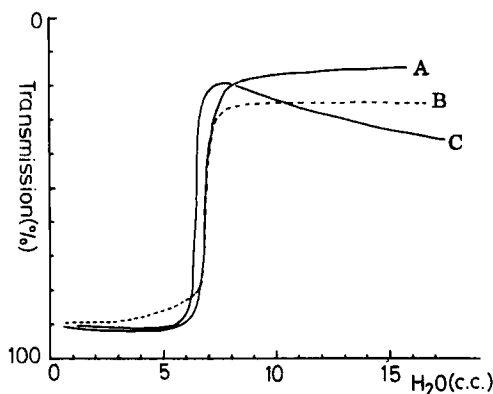


FIG. 4. Turbidimetries of graft, mixed polymer and PVC in 0.2% THF solutions. (A) Graft polymer (No. 5 in Table 3). (B) Mixed polymer with n-BA-AA (88.9:11.1 mole ratio) copolymer/PVC = 0.42. (C) PVC.

Kennedy et al. [19] reported that in the cationic graft polymer of PVC a endothermic peak at 270°C shifted to 326°C. The shift was ascribed to formation of short branching through elimination of tertiary chlorine and allyl-type chlorine. In the present photoinduced graft polymer, the appearance of the two peaks at 290 and 305°C may be ascribed to branching structures due to the following two schemes:

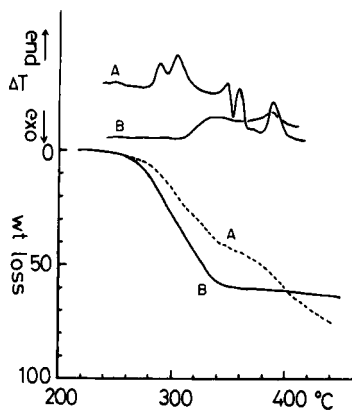
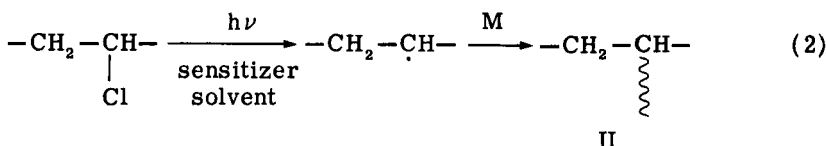
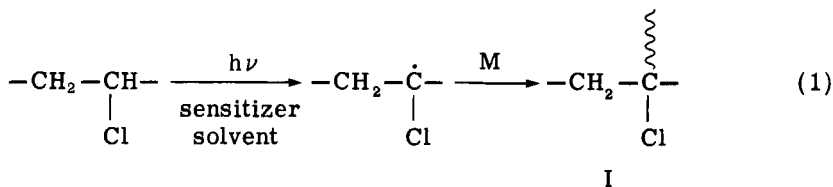


FIG. 5. DTA and TGA of graft polymer (No. 1 in Table 3) and PVC. (A) Graft polymer. (B) PVC.



Structures I and II have peaks at 290 and 305°C, respectively.

The acrylic acid unit content in the graft polymer was determined by the pH change with sodium hydroxide aq solution as shown in Fig. 6, and the analysis of branching in the graft copolymer of n-butyl acrylate-acrylic acid on PVC is tabulated in Table 4. From pH vs titrant (NaOH aq) curves in THF-water solution, as shown in Fig. 6, pK_a was estimated by using the Henderson equation [20-23].

$$\text{pH} = \text{p}K_a - n \log \frac{1 - \alpha}{\alpha} \tag{3}$$

where K_a is the dissociation constant and α is the degree of dissociation. The results are shown in Fig. 7. The relation between pK_a of the

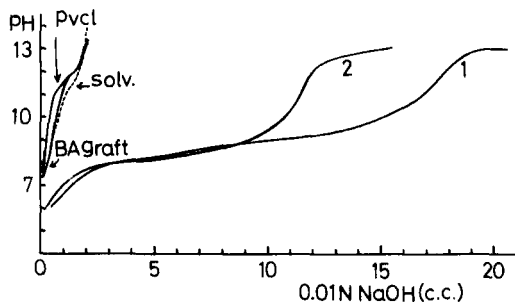


FIG. 6. Titration curves of graft polymers (Nos. 1 and 2 in Table 3) with aqueous NaOH. Initial polymer solutions were prepared by dissolving 0.1 g of polymer in THF (50 cc) and water (1 cc).

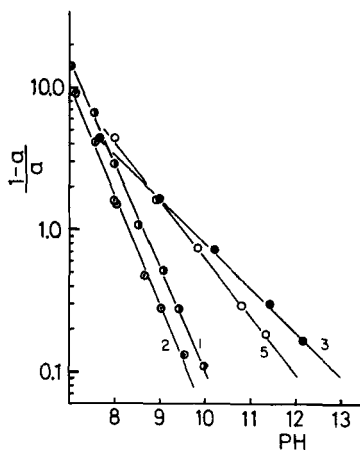


FIG. 7. Henderson plots of graft polymer solutions. Graft polymers of Nos. 1, 2, 3, and 5 in Table 3 were used. n was 1.30, 1.35, 3.15, and 2.40, respectively, for each sample.

acrylic acid unit with the content of the acid unit in the graft polymer is shown in Fig. 8. pK_a changes of the acrylic acid unit by graft

branching may be obtained by shielding the dissociation group (acrylic acid unit) by polymer-polymer interaction. That is, the lower acrylic acid unit content in the polymer showed the higher value of pK_a which

TABLE 4. Analysis of Branch in Graft Copolymer of n-Butyl Acrylate-Acrylic Acid on PVC^a

No. ^b	Monomer in feed		Polymer wt required for analysis (g)	NaOH (ml)	Acrylic acid unit content in graft polymer (mole/g)	Branch in graft copolymer	
	Acrylic acid (mole %)	n-Butyl acrylate (mole %)				Acrylic acid mole %	n-Butyl acrylate ^c (mole %)
1	30.62	69.38	0.1018	15.5 ^d	1.58×10^{-3}	26.87	73.13
2	29.25	70.75	0.1023	10.2	1.03×10^{-3}	34.21	65.79
3	25.63	74.37	0.1010	2.6	0.266×10^{-3}	14.03	85.97
5	25.14	74.86	0.1005	2.6	0.268×10^{-3}	11.13	88.87

^a A given quantity of graft copolymer was dissolved in 50 cc of tetrahydrofuran containing 1 cc of water, and its solution was titrated with 0.01035 N NaOH aq solution.

^b Same as in Table 3.

^c These values were evaluated from acrylic acid unit content in graft polymer and degree of grafting.

^d End points were determined by differential curves.

TABLE 5. Graft Copolymerization of *n*-Butyl Acrylate—Acrylic Acid on Carbon Monoxide—Vinyl Chloride Copolymer^a

No. (g)	Polymer (g)	Solvent (cc)	<i>n</i> -Butyl acrylate (cc)	Acrylic acid (cc)	Benzophenone (g)	Irradiation time (min)	Degree of grafting (%)	Grafting efficiency (%)
1	0.536	CY (6)	1.5	0.25	0.0172	105	0	0
2	0.532	DIO (5)	5	1	0.0384	50	99.2	12.3
3	0.773	DIO (5)	5	1	0.0360	120	98.2	15.8

^aCO unit content in carbon monoxide—vinyl chloride copolymer was 16.23 mole %, and graft copolymerization was carried out at 80°C.

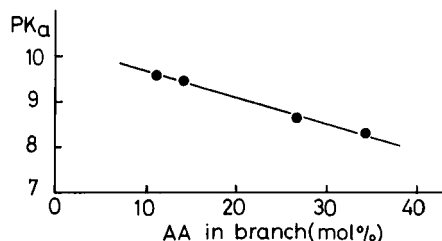


FIG. 8. Relation of pK_a with acrylic acid unit content in branch of graft copolymer.

was due to the difficulty of dissociation in the environment of the polymer chain.

If graft polymerization on PVC is initiated by abstraction of hydrogen or chlorine from the polymer molecule, as shown in Eqs. (1) and (2), a carbon monoxide-vinyl chloride copolymer that has a photosensitive carbonyl group in main chain will produce a graft polymer having a high degree of grafting. In fact, in this polymer a higher degree of grafting was obtained even in dioxane solution as shown in Table 5. We have previously shown that the rate of dehydrochlorination is about three times as large in carbon monoxide-vinyl chloride copolymer compared with PVC [24].

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Accepted by editor December 3, 1973

Received for publication December 19, 1973