

Copolymerization of Allylidene Diacetate and Styrene, and the Chemical Reactions of the Saponified Copolymer

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Copolymer of allylidene diacetate and styrene was prepared, whose composition was found by saponification value determination, elemental analysis and carbonyl number determination of the saponified copolymer.

The results of three methods agreed well. Then, the copolymer was saponified to prepare polymer having aldehyde groups along the main chain. By chain transfer mechanism, vinyl acetate was grafted to the aldehyde group of the acrolein copolymer. The graft copolymer composed of polyvinyl acetate branches and the acrolein copolymer was obtained.

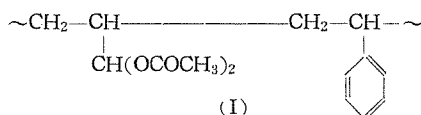
In addition, the aldehyde group of acrolein copolymer was reacted with diethyl maleate catalyzed by benzoyl peroxide.

It has been observed that the vinyl polymer having aldehyde groups along the main chain can be prepared by saponification of polyallylidene diacetate or of copolymers of allylidene diacetate.¹⁾⁻⁴⁾ Such polymers may be regarded superficially as the addition polymer of acrolein or its copolymer. But we have little work which deals with the chemical reaction of the aldehyde group of such polymers.

In the present work, copolymerization of allylidene diacetate and styrene was studied, and some chemical reactions of aldehyde group of the saponified copolymer were performed.

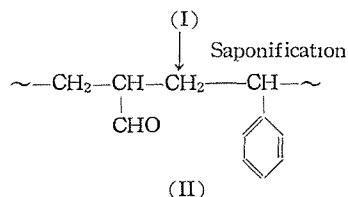
Allylidene diacetate (Aden DA) was copolymerized with styrene in benzene solution, and the composition of the copolymer was determined by saponification value and elemental analysis.

Copolymers which consisted of 8~10 % of AdenDA unit and 90~92 % of styrene unit were obtained. Then, vinyl polymer having aldehyde groups along the main chain was obtained (II) by the saponification of the copolymer (I) with alcoholic potash in dioxane.

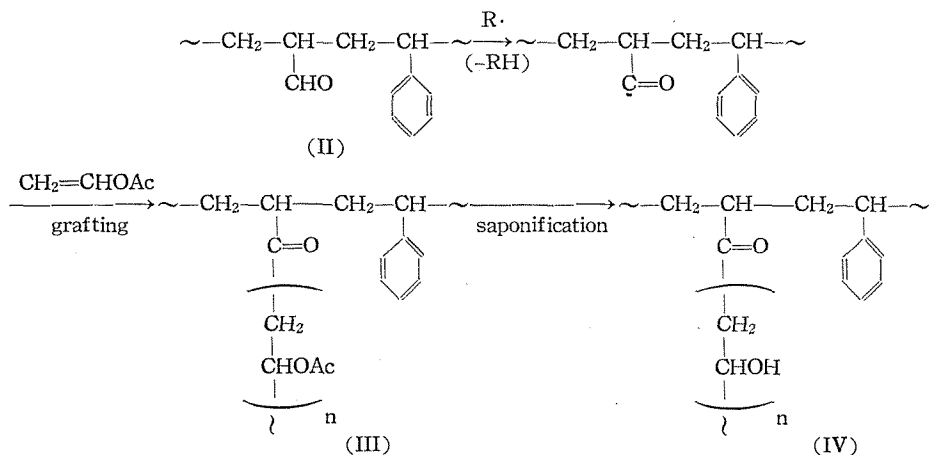


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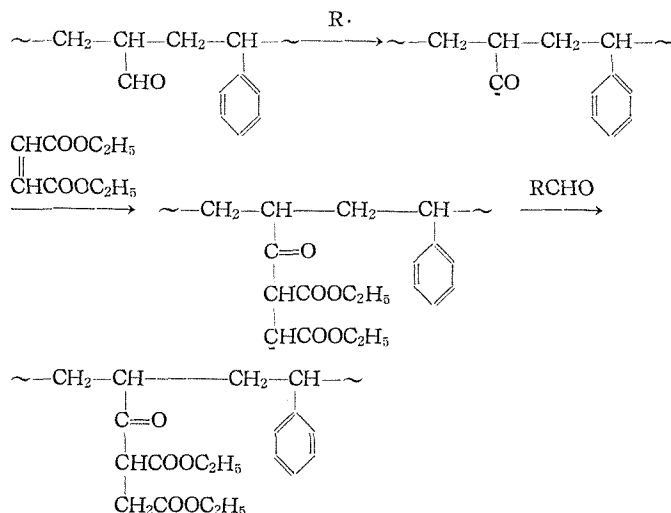


Some chemical reactions were carried out on the aldehyde group of the polymer (II). It is well-known that the hydrogen atom of aldehyde group is easily abstracted by a free radical, and that aldehyde is a potent chain transfer agent in free radical polymerization of vinyl compound.⁵⁾ When the aldehyde group of the polymer (II) acts as chain transfer, so-called "graft copolymer"⁶⁾ will be produced, i.e., radicals generated along main chain by hydrogen abstraction of aldehyde groups would initiate the polymerization of certain monomer. In the present study, vinyl acetate was polymerized by benzoyl peroxide in the presence of the acrolein copolymer (II).



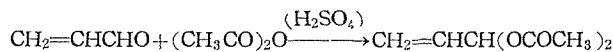
The total gross polymer obtained may be a mixture of the graft copolymer (III), straight polyvinylacetate and the aldehyde polymer which has not been grafted. The latter two polymers were removed from the total gross polymer by the following procedure. The ungrafted polymer (II) was soluble in ethyl ether while the other two were not, and it was removed by ether-extraction. Straight polyvinylacetate was made soluble in hot water by saponification, which was removed by extraction with water. Having been saponified, the graft copolymer (IV) was soluble neither in benzene nor in hot water.

The second reaction adapted to the aldehyde group of the polymer (II) is that with diethylmaleate. In general, aldehyde reacts with maleic ester to form acylsuccinate in the presence of radical producing catalyst⁷⁾. The acrolein polymer (II) was found to add diethyl maleate in the presence of benzoyl peroxide.



EXPERIMENTAL RESULTS

(1) Synthesis of AdenDA



To 159 g. of acetic anhydride containing 1 c.c. of sulphuric acid, 75 g. of acrolein was added dropwise under cooling by ice-salt (at $-10^\circ \sim -3^\circ\text{C}$) during one hour, and the reaction mixture was kept at 0°C for two hours. Then the reaction mixture was poured on 100 g. of ice containing 3 g. of hydrochloric acid. The oily layer separated, and the aqueous layer was extracted with ether. The oily layer together with ether extract was washed with Na-bicarbonate solution, Na-bisulphite solution and water successively, and was dried over anhydrous sodium sulphate. On distillation of the ether solution, 120 g. of AdenDA was obtained at $67^\circ\text{C}/8\text{ mmHg}$. Yield calculated on acrolein : 57 %.

(2) Copolymerization of AdenDA and styrene

The following procedure was adopted. To the benzene solution of AdenDA, a small quantity of styrene was added at intervals of a fixed time. A typical experiment is as follows:

To the mixture of 63.2 g. (0.4 M) of AdenDA and 60 c.c. of benzene which was being kept at 80°C , 4.16 g. of styrene (0.04 M) and 0.1 g. of azobisisobutyronitrile were added under stirring at every two hours. After 10 times' addition of styrene (20 hours), the reaction mixture was heated for additional 2 hours. Then the reaction mixture was filtered through a glass filter and added dropwise to 500 c.c. of methanol under stirring. The precipitated polymer was dissolved in acetone, precipitated in methanol again in vacuo. The polymer thus purified was 25.4 g. (SA-7). The copolymer

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was soluble in acetone, dioxane and ethyl ether, and insoluble in methanol and water.

(3) Analysis of copolymer

The copolymer was analyzed by saponification value determination and elemental analysis. Results of the two methods agreed well and they were in accord with the result of the carbonyl number determination of the saponified polymer, which is to be shown in the following section.

Saponification value determination About 0.2 g. of the sample was dissolved in 10 c.c. of solvent, and 10 c.c. of 0.5 N-KOH in ethanol was added. After saponification, 10 c.c. of 0.5 N-H₂SO₄ was added to the reaction mixture and excess acid was titrated with 0.1 N-NaOH. Blank test was made under the similar condition. The content of AdenDA unit was calculated from the difference of the amount of alkali used in two experiments. The saponification value of pure polyallylidenediacetate prepared by polymerization of AdenDA was determined under various conditions. Results are shown in table 1.

Table 1 shows that good results were obtained by saponification at room temperature, while somewhat larger values were obtained at higher temperatures. The larger values may be ascribed to carboxylic group which might be formed by the interaction between aldehyde groups.

Table 1. Saponification value determination of poly AdenDA.

Expt. no.	Sample (g)	Saponification		Difference of titration (eq. $\times 10^4$)	% *
		Temp.	Time		
11	0.2008	Reflux	1 hr.	26.11	102.3
12	0.2003	Room temp.	3 days	25.32	99.92
13	0.2012	60~70°C	4 hrs.	26.06	102.3
15	0.1997	Room temp.	1 day	25.02	99.0

* Percentage to the calculated value of pure polyallylidenediacetate.

Saponification values of copolymers, SA-1, SA-4 and SA-7, which were prepared by a similar procedure to the above mentioned with slight modification, were determined. Results are listed in Table 2.

Elemental analysis The following results were obtained, which were in good agreement with calculated values from the saponification value determination.

[SA-1] Calcd. for 7.85 % of AdenDA unit : C, 87.81 % : H, 7.535 % : Found : C, 87.83 % : H, 7.743 %.

[SA-4] Calcd. for 10.50 % of AdenDA unit : C, 86.11 % : H, 7.49 % : Found : C, 86.29 % : H, 7.49 %.

Table 2. Saponification value determination of Copolymer.

Expt. No.	Sample		Saponification		Difference of titration (eq. $\times 10^4$)	AdenDA unit %
	Copolymer	(g)	Temp.	Time		
14	SA-1	0.4003	Reflux	1 hr.	4.45	5.97
17	SA-1	0.4019	Room temp.	1 day	5.84	7.85
22	SA-4	0.2916	Room temp.	1 day	5.58	10.50
24	SA-4	0.2000	60°~70°C	4 hrs.	4.64	12.86
28	SA-7	0.2003	60°C	4 hrs.	2.73	7.87
29	SA-7	0.2008	60°C	4 hrs.	2.71	7.81
30	SA-7	0.2000	Room temp.	2 days	2.62	7.63

* The number of AdenDA unit per 100 units.

[SA-7] Calcd. for 7.87 % of AdenDA unit : C, 87.80 % : H, 7.53 % : Found : C, 87.62 % : H, 7.56 %.

(4) Saponification of copolymer

To 15 g. of copolymer (SA-7) in 90 c.c. of dioxane, 2.5 g. of potassium hydroxide in 20 c.c. of ethanol was added. The reaction mixture was kept at room temperature for 3 days, and then it was added to 500 c.c. of methanol under stirring after filtration through a glass filter. The precipitated polymer was washed with water, dissolved in dioxane again. The polymer thus purified was dried in vacuo. The polymer obtained (SA-8) was 12.25 g.

(5) Carbonyl-number determination of the saponified polymer

Saponified polymer (SA-8) which was obtained from the copolymer (SA-7) was subjected to carbonyl number determination by hydroxylamine- H_2SO_4 method⁸⁾. To about 0.2 g. of the sample dissolved in 10 c.c. of dioxane, 2 c.c. of 0.5N-solution of hydroxylamine- H_2SO_4 in water was added. The reaction mixture was heated at 65°C for 4 hours with occasional shaking. The mixture was poured in 50 c.c. of water, and the precipitated polymer was removed by filtration through a glass filter. The aqueous filtrate together with the aqueous washings was titrated with 0.1N-NaOH using the mixed indicator of methyl-orange and indigocarmine. Blank test was made under the same condition. The carbonyl number was calculated from the difference of the amount of alkali used in sample and blank experiments. Duplicate experiments were made, and 8.12 % and 8.07 % of $-\text{CH}_2-\text{CH}(\text{CHO})-$ unit were found. They are in agreement with the results obtained in the saponification value determination and in elemental analysis. Furthermore the carbon and hydrogen contents calculated for 8.09 % (average $-\text{CH}_2-\text{CH}(\text{CHO})-$ unit percentage) of AdenDA unit agree with the result of the elemental analysis, i.e.,

Calcd : C, 87.69 % : H, 7.53 %.

Found : C, 87.62 % : H, 7.56 %.

(6) Graft copolymerization

The saponified polymer (SA-8) consisting of 92 % of styrene unit and 8 % of acrolein unit was grafted with vinyl acetate. The saponified polymer was dissolved in 10 c.c. of benzene, and 10 c.c. of vinyl acetate and 0.100 g. of benzoyl peroxide were added. In a sealed tube the mixture was heated at 70°C for 7 hours. Then the contents was poured in 500 c.c. of ethyl ether. The ether soluble polymer was obtained by precipitation in methanol, which was found to be ungrafted polymer (SA-8) by saponification value determination. The ether insoluble polymer may be the mixture of straight polyvinylacetate and the graft polymer (III) consisting of SA-8 as back-bone and of polyvinyl acetate as branches. Separation of these two polymers was performed as follows. The ether insoluble mixture (polymer C) was saponified by reflux with alcoholic potash in benzene for 2 hours. The precipitated polymer was collected on a glass filter, and dried in vacuo (polymer D). Polymer washed with methanol D was extracted with hot water. Polyvinylalcohol which might result from straight polyvinylacetate was extracted with hot water, and it was isolated by precipitation in methanol (polymer E). The water insoluble polymer (polymer F) may be regarded as graft copolymer because it was soluble neither in benzene nor in water.

In some cases graft copolymers consisting of oil soluble part and water soluble part are soluble both in benzene and water⁹⁾, while in other cases they are insoluble neither in benzene nor in water¹⁰⁾. This discrepancy may be ascribed to the properties and the relative amounts of two parts. It is evident that the graft copolymer formed in the present study belongs to the latter.

The grafting reaction may be caused by radical transfer of aldehyde group as was cited previously. But the possibility of chain transfer reaction on α -carbon atom of phenyl group of styrene unit has not been excluded. In order to examine the latter possibility, blank experiment was carried out, i.e., straight polystyrene was added instead of acrolein copolymer. After polymerization of vinyl acetate under the same condition as in the case of acrolein copolymer, polystyrene was recovered without any measurable loss as the precipitant in methanol, and no water-insoluble polymer was obtained when the methanol soluble polymer (polyvinylacetate) was saponified. This fact definitely indicates that no graft reaction occurred on α -carbon atom of styrene unit, and this conclusion is in agreement with that of G. Smets¹¹⁾.

The graft copolymer thus obtained was acetylated by the method which is essentially the same as that described in the acetylation of polyvinylalcohol¹²⁾. The graft copolymer became benzene-soluble. The amount of polyvinylacetate branches of the acetylated graft copolymer was calculated from the result of its saponification value determination. The water soluble polymer (polymer E) was acetylated by the manner

mentioned above, and the acetylated polymer was subjected to saponification value determination. The value was 101.5 % of that calculated for pure polyvinylacetate. This apparently shows that the water soluble polymer was almost pure polyvinylalcohol.

The separation procedures described above are summarized in the following scheme and the quantitative results are shown in tables 3, 4 and 5.

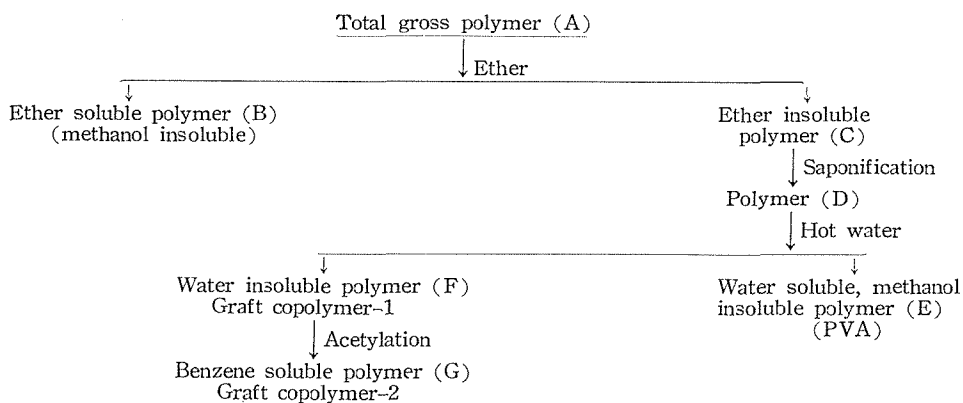


Table 3. Graft copolymerization (1).

Tube no.	Acrolein copolymer (SA-8) added (g)	Total gross polymer (A)		Polymzn. (%)	Ether soluble polymer (B)		Ether insoluble polymer (C)	
			(g)			(g)		(g)
2	1.000	G-12-A	6.489	59	G-12-B	0.564	G-12-C	6.003
3	2.000	G-13-A	7.129	55	G-13-B	1.077	G-13-C	6.128
4	4.000	G-14-A	7.841	41	G-14-B	2.853	G-14-C	5.048

Table 4. Graft copolymerization (2).

Tube no.	Polymer D (g)	Polymer E (g)	Polymer F (g)	Acetylated graft copolymer (G)	
				Back bone (SA-8) (g)	Branch (PVAc) (g)
2	3.481	2.588	0.893	0.436	0.794
3	3.703	1.743	1.960	0.923	2.025
4	2.980	1.035	1.945	0.996	1.895

Table 5. Graft copolymerization (3).

Tube no.	Acrolein copolymer (SA-8) added (g)	Ungrafted		Grafted	
		Polymer B (g)	%	in polymer G (g)	%
2	10.00	0.564	56.4	0.436	43.6
3	2.000	1.077	53.8	0.923	46.2
4	4.000	2.853	71.3	0.996	24.9

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As is shown in tables 3 and 4, the amount of back-bone part of the acetylated graft copolymer (G) obtained in tube 4 was 0.996 g. and that of the ungrafted polymer (B) was 2.853 g. The sum of two amounts is 3.849 g, which is 96.2 % of that of the acrolein copolymer (SA-8) originally added (4.000 g.). This result may be taken to indicate the validity of the separation procedure. With regard to the graft copolymers (F) obtained in tubes 2 and 3, acetyl values were not determined. Their compositions were calculated from the material balance of SA-8, i.e., the amount of the backbone part of the graft copolymer was regarded as the difference of the amount of acrolein copolymer added (SA-8) and that of the ether-soluble polymer (B). The relative amount of the grafted SA-8 to the ungrafted SA-8 (E) in three tubes are listed in table 5.

(6) Reaction with diethyl maleate

The homogeneous solution of 1.0025 g. of acrolein copolymer (SA-8), 5.0 g. of diethyl maleate and 0.100 g. of benzoyl peroxide in 10.0 c.c. of benzene (dry and thiophene-free) was refluxed for 35 hours. During reflux 50 mg. of benzoyl peroxide was added at every 7 hours for 4 times. The reaction mixture was added to about 350 c.c. of methanol, and the precipitated polymer, having been dried, was dissolved in dioxane and precipitated in methanol again. The polymer was subjected to the determination of saponification value after it had been purified by 4 times' reprecipitation. About 0.2 g. of the polymer was dissolved in 10 c.c. of dioxane, and 10 c.c. of 0.5N-NaOH in ethanol was added. After one hour's heating at 65°C, 10 c.c. of 0.5N-H₂SO₄ was added, and the excess acid was titrated with 0.1N-NaOH. ($f=1.134$). The blank test was carried out on SA-8. The amount of acylsuccinate group attached to the polymer was calculated from the difference of alkali used in sample and blank experiments. It was found that one aldehyde group per 2.57 group reacted with diethyl maleate.

SUMMARY

1. Copolymer of allylidenediacetate and styrene was prepared, whose composition was found by saponification value determination, elemental analysis and the carbonyl number determination of the saponified copolymer. The results of these three methods agreed well.
2. The copolymer was saponified to prepare the polymer which has aldehyde groups along the main chain.
3. Vinyl acetate was grafted to the aldehyde group attached to the polymer. The graft copolymer composed of polyvinylacetate branches and saponified acrolein copolymer back-bone. The saponified graft copolymer was soluble neither in benzene nor in water.
4. The aldehyde group of acrolein copolymer was reacted with diethylmaleate catalyzed by benzoyl peroxide.

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