

Polymer Structure Formed in Radiation-Induced Graft Polymerization. II

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Synopsis

Methyl methacrylate was grafted onto viscose rayon, wood pulp, cellophane, and poly(vinyl alcohol) with preirradiation techniques using γ -rays from a Co-60 source, and the stereoregularities of the grafted polymers separated from the trunk polymers and homopolymers were determined. The stereoregularity of the polymers grafted onto rayons is different from that of the polymers grafted onto wood pulp, mercerized wood pulp, cellophane, and poly(vinyl alcohol), confirming our previous results.

INTRODUCTION

In our previous paper,¹ we have reported that the stereoregularity of poly(methyl methacrylate) (PMMA) and poly(methacrylic acid) (PMAA) grafted onto viscose rayon and cotton was different from that of the polymers formed in ordinary radical polymerization, whereas the stereoregularity of PMMA and PMAA grafted onto nylon, polyester fibers, and cellulose acetate fibers is the same as that of the ordinary polymers.

In this paper, the results of grafting of methyl methacrylate onto hydrophilic polymers are presented and discussed. The trunk polymers used as hydrophilic polymers were poly(vinyl alcohol) (PVA) film, PVA powder, viscose rayon, cellophane, and wood pulp. Furthermore, the influence of activation, mercerization, and addition of chain transfer agent in the polymerization system was investigated.

EXPERIMENTAL

Materials

Methyl methacrylate was purified by the usual procedure. PVA used as the trunk polymer was in the form of powder ($P_n = 2400$) or films 0.03 mm thick which were prepared from the PVA powder by casting from hot water solutions.^{2,3} Viscose rayon used as the trunk polymer is staples of high-tenacity type (Kanelion, 1.5 d \times 32 mm). Wood pulp is of a viscose rayon grade made from hardwoods (sulfite pulp, D.P. = 700).

The wood pulp and viscose rayon were purified by Soxhlet extraction with methanol and acetone as solvent and dried in vacuo.

In order to enhance the grafting reaction, wood pulp and viscose rayon were activated by immersing in water, then replacing with acetone-water, gradually increasing the concentration of acetone in the aqueous solution.

The mercerization of wood pulp was carried out by treating the pulp with 20% NaOH solution for 1 hr at room temperature, followed by washing with distilled water and drying in vacuo.

Graft Polymerization

The trunk polymers (0.3 or 0.5 g) were placed in glass ampoules and then irradiated by γ -rays from a Co-60 source at 0°C in the presence of air (dose rate, 1.3×10^5 – 2.2×10^5 rad/hr; irradiation time, 17–20 hr). After the irradiation, monomer solution (50 vol-%) in methanol was poured into the ampoule and kept in a Dry Ice-ethanol bath (–78°C). The graft polymerization was then carried out at 60°C after the ampoule was sealed under reduced pressure.

After the polymerization, the contents were poured into methanol to precipitate the polymer. Then the graft copolymer was separated from the homopolymer by Soxhlet extraction with chloroform for 48 hr. The graft copolymer was dried in vacuo and the weight increase was determined.

The grafted polymer (branch polymer) was then isolated from the trunk polymer by acid hydrolysis or oxidation. The graft copolymers onto cellophane, pulp, and rayon were isolated by hydrolysis in 50% H₂SO₄ for two days at room temperature. The graft copolymers onto PVA were isolated by oxidation of the trunk polymer with 30% HNO₃ for two days at room temperature.⁴ After hydrolysis or oxidation of the trunk polymers, PMMA residue was dissolved in chloroform and then precipitated with methanol.

Characterization of Polymers

The tacticities of the PMMA obtained were determined by ¹H-NMR spectroscopy. NMR measurement was carried out at 120°C by means of a Japan Electron Optics Laboratory 100-MHz PS-100 spectrometer on CD₃NO₂ solutions (5–10%) with tetramethylsilane as reference.

RESULTS AND DISCUSSION

In our previous paper,¹ the stereoregularity of PMMA grafted onto viscose rayon and cotton is different from that of PMMA grafted onto hydrophobic fibers and that of radically prepared polymers. Therefore, this study was carried out to investigate whether the hydrophilicity of trunk polymers is important in influencing the stereoregularity of the grafted polymers.

The results of the graft polymerization of MMA onto cellophane and pulps are shown in Table I.

In the case of the graft polymerization of MMA onto pulp, the degree of grafting and graft efficiency decreased as expected with the addition of chain transfer agent. When activated pulp was used as the trunk polymer, the degree of grafting and the weights of the grafted polymer and the homopolymer

TABLE I
Results of Graft Polymerization of Methyl Methacrylate
onto Cellophane and Wood Pulps

Sample	Cellophane	Pulp	Pulp	Activated pulp	Mercerization	
					Pulp	Activated pulp
Weight of sample, g	0.528	0.548	0.312	0.300	0.307	0.316
Monomer solution, ml	20	20	16	16	16	16
<i>n</i> -BuSH, μ l	5	5	—	—	—	—
Polymerization time, hr	22	22	3	3	3	3
Total weight, g	3.924	3.158	2.214	0.542	2.916	3.478
Grafted polymer, g	0.718	0.274	1.148	0.170	1.628	2.007
Homopolymer, g	2.678	2.336	0.754	0.072	0.981	1.155
Degree of grafting, %	136.1	50.0	367.8	56.7	529.5	635.3
Graft efficiency, %	21.2	10.5	60.4	70.2	62.4	63.5

TABLE II
Stereoregularity of Poly(methyl Methacrylates) Grafted
onto Cellophane and Wood Pulps^a

	Cellophane ^b		Pulp ^b		Pulp		Activated pulp		Mercerization				Ordinary BPO-initiated polymer
									Pulp		Activated pulp		
	G	H	G	H	G	H	G	H	G	H	G	H	
S	62.9	64.3	62.6	64.9	62.3	62.6	61.6	65.7	61.0	61.3	59.9	61.3	62.0
H	33.3	32.1	33.5	32.1	34.1	33.2	35.0	31.0	34.3	35.1	35.3	34.6	33.8
I	3.8	3.6	3.9	3.0	3.6	4.2	3.4	3.3	4.7	3.6	4.8	4.1	4.2

^a G = Grafted polymer; H = homopolymer.

^b With added *n*-BuSH.

were found to decrease, indicating that no enhancement of grafting reactions was resulted by activation treatment. This fact is also found in the case of activated rayon. The results may be ascribed mainly to the decrease of stable radical concentration formed by γ -ray irradiation in the activated pulps. In the case of the mercerized pulps, the degree of the grafting increased remarkably, but the graft efficiency is not affected.

The stereoregularities of PMMA's grafted onto cellophane or pulps are shown in Table II. As is evident from the table, the stereoregularities of the grafted polymers and homopolymers are almost the same as that of the polymer formed in ordinary radical polymerization when the experimental error is taken into consideration. It seems that the addition of chain transfer agent, activation treatment, and mercerization have no effect on the stereoregularity of the polymers formed.

The results of the graft polymerization of MMA onto PVA and rayons are shown in Table III. In the case of PVA powder, the degree of grafting and the graft efficiency decreased with addition of *n*-butyl mercaptan. In the case of PVA film, the degree of grafting is large, even with the addition of *n*-butyl mercaptan, although the graft efficiency is low. When rayon was used as trunk polymer, the degree of grafting and graft efficiency are considerably high, indicating a similar tendency to those of PVA powder and wood pulps. In the case of activated rayon as the trunk polymer, the degree of grafting and the graft efficiency decreased as for the activated pulp.

The stereoregularities of PMMA's grafted onto PVA or rayons are shown

TABLE III
Results of Graft Polymerization of Methyl Methacrylate
onto Poly(vinyl Alcohol) and Rayons

Sample	PVA powder	PVA film	PVA powder	Rayon	Activated rayon	Activated rayon
Weight of sample, g	0.538	0.569	0.344	0.362	0.311	0.508
Monomer solution, ml	20	20	16	16	16	20
<i>n</i> -BuSH, μ l	5	5	—	—	—	5
Polymerization time, hr	22	22	3	3	3	22
Total weight, g	1.793	4.789	1.596	1.146	0.430	1.673
Grafted polymer, g	0.281	1.432	0.855	0.655	0.061	0.350
Homopolymer, g	0.974	2.788	0.397	0.129	0.058	0.815
Degree of grafting, %	52.3	251.2	247.8	180.5	19.6	68.9
Graft efficiency, %	22.4	33.9	68.3	83.5	51.6	30.0

TABLE IV
Stereoregularity of Poly(methyl Methacrylates)
Grafted onto Poly(vinyl Alcohol) and Rayons^a

	PVA powder ^b		PVA film ^b		PVA powder		Rayon		Activated rayon		Activated rayon ^b		Ordinary BPO-initiated polymer
	G	H	G	H	G	H	G	H	G	H	G	H	
S	65.4	63.5	63.3	63.6	63.2	63.8	54.5	58.1	58.6	63.0	54.7	63.5	62.0
H	32.0	33.3	33.9	33.5	33.2	32.7	39.2	36.6	36.5	33.7	39.5	33.2	33.8
I	2.6	3.2	2.8	2.9	3.6	3.5	6.3	5.3	4.9	3.5	5.8	3.3	4.2

^a G = Grafted polymer; H = homopolymer.

^b With added *n*-BuSH.

in Table IV. Although it seems that the stereoregularities of PMMA grafted onto PVA powder and film were a little different, that is, larger in syndiotacticity and lower in isotacticity than those of the polymer formed in ordinary radical polymerization, it is not yet definite that this difference is significant.

In the case of rayon, irrespective of the addition of chain transfer agent or activation treatment, increases in isotacticity and heterotacticity and a large decrease in syndiotacticity were clearly observed for the grafted polymers. This results confirmed our previous data.

Since mercerized pulps and cellophane have cellulose II structure as well as rayon, the crystalline structure of cellulose has no effect on the stereoregularity of the grafted polymers. The fact that the stereoregularity of the polymers grafted onto rayon and cotton is different from that of polymers grafted onto wood pulp, mercerized wood pulp, and PVA shows that neither the hydrophilicity of the trunk polymer nor the crystalline structure of cellulose is the determining factor for the stereoregularity of the grafted polymers. The results may indicate that the structure of location where grafting reaction occurs, such as pore size and the supermolecular structure of pores, etc., are important for determining the stereoregularity of the grafted polymers.

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