

Polymer Structure Formed in Radiation-Induced Graft Polymerization

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Synopsis

Methacrylic acid (MAA) and methyl methacrylate (MMA) were grafted onto nylon 6, cellulose triacetate, cotton, viscose rayon, and polyester fibers, and the stereoregularities of the grafted polymers were determined. The graft polymerization was carried out with preirradiation techniques using γ -rays from a Co 60 source. The grafted copolymers were then separated from the homopolymers by Soxhlet extraction. The grafted (branch) polymers were isolated from the trunk polymers by acid hydrolysis and their stereoregularity was determined with a 100 MHz NMR spectrometer. The stereoregularity of PMAA or PMMA grafted onto viscose rayon or cotton fiber was different from that of the polymers formed in ordinary radical polymerization.

INTRODUCTION

Many studies on the graft copolymerization of vinyl monomers onto various polymers have been carried out,¹⁻⁶ but only a few studies on the stereoregularities of the grafted polymers have been reported.⁷⁻¹⁰ In those reports, however, no quantitative studies on the stereoregularities have been made. The stereoregularities of the grafted polymers onto the fibers are expected to be different from those of the ordinary radical-initiated polymers, because the structures of the fibers would have some influence on the molecular association and orientation of the monomers being polymerized. This investigation was carried out according to this concept.

EXPERIMENTAL

Materials

The monomers, methacrylic acid (MAA) and methyl methacrylate (MMA), were purified by the usual procedures.

The fibers used as trunk polymers was nylon 6 (70 denier, 24 filaments, continuous bright yarn), cellulose triacetate (75 denier, 20 filaments, continuous bright yarn, acetic acid content 61.1%), viscose rayon (high-tenacity staple fiber for textiles), surgical cotton, and polyester (75 denier, 36 filaments, continuous bright yarn).

The continuous-filament yarns were cut into about 7-cm lengths. The fibers were purified by Soxhlet extraction with ether and ethanol as solvents, each for 7 hr, and dried in vacuo.

Graft Polymerization

The fibers (0.3 or 1.0 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: 1.5×10^6 rad/hr, irradiation time: 17 hr). After the irradiation, a monomer solution (50 vol-%) in methanol or dimethyl sulfoxide (for polyester fibers) was poured into the ampoule kept in a Dry Ice-isopropanol 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 ether [for poly(methacrylic acid) (PMAA)] or *n*-hexane [for polymethyl methacrylate (PMMA)] to precipitate the polymer. Then the graft copolymer was separated from the homopolymer by Soxhlet extraction with methanol (for PMAA) or benzene (for PMMA) for 96 hr. The graft copolymer was dried in vacuo and the weight increase was determined.

Then the grafted polymer (branch polymer) was isolated from the trunk polymer by acid hydrolysis. The graft copolymers onto nylon 6, viscose rayon, and cellulose triacetate fibers were hydrolyzed by refluxing in 6*N* HCl aqueous solutions after swelling in dioxane for several hours at room temperature. The graft copolymers onto cotton and polyester fibers were hydrolyzed in 50% and 75% H₂SO₄, respectively, for one to two days at room temperature.

After hydrolysis of the trunk polymer, the PMAA residue was dissolved in methanol and the PMMA residue was dissolved in acetone. The solutions were then precipitated with ether and *n*-hexane, respectively. Furthermore, all the polymers were purified by redissolving them in methanol and benzene, respectively, and reprecipitating with ether and *n*-hexane, respectively.

The purified PMAA was then methylated to PMMA by diazomethane.

Characterization of Polymers

The tacticities of the PMMA obtained were determined by NMR spectroscopy. PMMA was dissolved in nitromethane to give a 5–10% solution. NMR measurement was carried out at 120°C by means of a Japan Electron Optics Laboratory 100-MHz spectrometer.

Viscosities of PMMA were measured on acetone solutions at 30°C.

RESULTS AND DISCUSSION

This study was carried out to investigate if the stereoregularity of the grafted polymer onto the fiber differs from that of the radical-initiated polymer owing to the influence of the fiber structure. To examine the influence of fiber structure it seemed important that the degree of grafting

TABLE I
Results of Graft Polymerization of Methacrylic Acid

Fiber	Nylon 6	Cellulose triacetate	Viscose rayon	Cotton	Polyester
Weight of fiber, g	0.3016	0.2947	1.0174	1.0080	1.0669
Polymerization time, hr	24	24	24	24	24
Solvent	methanol	methanol	methanol	methanol	dimethyl sulfoxide
Monomer solution, ml	16	16	40	40	40
Grafted polymer, %	2.3	2.0	0.9	1.5	0.0
Homopolymer, %	1.1	2.1	0.9	3.7	0.4
Degree of grafting, %	61.6	54.2	17.3	30.1	0.1
Graft efficiency, %	68.1	48.1	50.2	28.5	0.8

be not too large. Therefore, we tried to obtain the proper degree of grafting by varying the graft polymerization time.

The results of the graft polymerization of MAA onto the fibers are shown in Table I, which indicates that the degree of grafting varied from 17.3% to 61.6% with a constant polymerization time of 24 hr. The graft polymerization of MAA onto polyester fibers hardly took effect, in spite of the presence of a swelling agent (dimethyl sulfoxide).

It is seen from Table II, which shows the results of the graft polymerization of MMA onto the fibers, that the degree of grafting varied from 16.3% to 134.3% with a graft polymerization time of 1.5–3 hr.

The viscosities (the molecular weight) and the stereoregularities of the grafted polymers and homopolymers are shown in Tables III and IV. Typical NMR spectra of the grafted polymers are shown in Figure 1. As is obvious from Table III, the stereoregularities of PMAAs grafted onto nylon 6 or cellulose triacetate fiber are almost the same as that of the polymer formed in ordinary radical polymerization when the experimental error (1–2%) is taken into consideration. On the contrary, when viscose rayon or cotton fiber was used as the trunk polymer, an increase in isotacticity and heterotacticity and a large decrease in syndiotacticity

TABLE II
Results of Graft Polymerization of Methyl Methacrylate

Fiber	Nylon 6	Cellulose triacetate	Viscose rayon	Cotton	Polyester
Weight of fiber, g	0.3284	0.3043	0.3562	0.3200	0.3147
Polymerization time, hr	1.5	2.0	3.0	3.0	3.0
Solvent	methanol	methanol	methanol	methanol	dimethyl sulfoxide
Monomer solution, ml	16	16	16	16	16
Grafted polymer, %	5.9	0.7	2.6	1.0	1.1
Homopolymer, %	3.0	2.3	1.2	3.3	12.0
Degree of grafting, %	134.3	16.3	59.3	23.6	26.2
Graft efficiency, %	66.0	22.0	54.2	23.6	8.3

TABLE III
Viscosity and Stereoregularity of Poly(methacrylic Acid)^a

	Nylon 6		Cellulose triacetate		Viscose rayon		Cotton		Polyester		Ordinary BPO-initiated polymer
	G	H	G	H	G	H	G	H	G	H	
Viscosity $[\eta]$	0.89	—	0.46	0.84	0.29	0.42	0.57	0.99	—	—	—
Molecular weight $\times 10^{-5}$	6.4	—	2.5	5.9	1.3	2.2	3.3	8.1	—	—	—
I, %	4.4	3.0	2.6	3.8	9.1	2.9	3.1	4.7	—	—	4.2
H, %	33.9	30.6	33.0	30.8	44.5	32.9	39.3	37.9	—	—	33.3
S, %	61.7	66.4	64.4	65.4	46.4	64.2	52.6	57.4	—	—	62.0

^a G = Grafted polymer; H = homopolymer.

TABLE IV
Viscosity and Stereoregularity of Poly(methyl Methacrylate)^a

	Nylon 6		Cellulose triacetate		Viscose rayon		Cotton		Polyester		Ordinary BPO-initiated polymer
	G	H	G	H	G	H	G	H	G	H	
Viscosity $[\eta]$	2.0	0.80	0.60	0.50	0.32	—	—	0.35	—	0.53	—
Molecular weight $\times 10^{-5}$	20	5.5	3.6	2.8	1.5	—	—	1.7	—	3.0	—
I, %	3.6	3.1	2.1	4.3	7.3	3.0	4.2	3.0	3.7	2.7	4.0
H, %	35.1	33.6	34.5	33.3	43.6	33.2	41.7	32.1	36.7	33.5	34.2
S, %	61.3	63.3	63.4	62.4	49.1	63.8	54.1	64.9	59.6	63.8	61.8

^a G = Grafted polymer; H = homopolymer.

were observed for the grafted polymer, clearly indicating that their stereoregularities differed from that of the radical-initiated polymer.

Table IV indicates that the stereoregularities of PMMAs grafted onto nylon 6, cellulose triacetate, or polyester fibers are almost the same as that of the ordinary polymer. The stereoregularities of the PMMAs, grafted onto viscose rayon or cotton, however, show similar tendency to those of PMAAs grafted onto the same fibers. On the other hand, all the homopolymers formed in the course of graft polymerization were found to have stereoregularities comparable with that of ordinary radical initiated polymer.

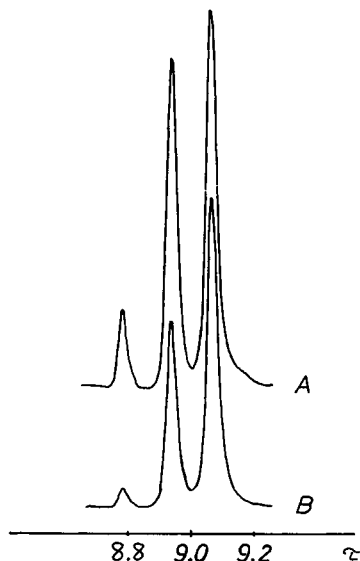


Fig. 1. NMR spectra of grafted polymers [poly(methyl methacrylate)] onto viscose rayon and nylon 6 fibers: (A) viscose rayon G; (B) nylon 6 G (Table IV).

It is apparent from Tables III and IV that the stereoregularities of the grafted polymers formed in the graft polymerizations onto some fibers clearly differ from that of ordinary radical-polymerized polymers, indicating that the structures of the polymers formed in the matrices of the fiber structures were influenced by the structures of the fibers. It seems, however, that the properties and the structures of the fiber matrices have a great effect on the stereoregularity of the polymers formed in the matrices.

The stereoregularity of the grafted polymer onto viscose rayon or cotton fiber is different from that of the grafted polymers obtained when nylon 6, cellulose triacetate, or polyester fiber was used as the trunk polymer, which is almost the same as that of the ordinary radical-initiated polymer. That is to say, the stereoregularities of the polymers grafted onto fibers that have hydrophobic groups are the same as those of ordinary polymers, but when viscose rayon or cotton fiber, which have hydrophilic groups,

is used as trunk polymer, the stereoregularity of the grafted polymer clearly differs from that of the ordinary radical-initiated polymer.

Therefore, the hydrophobicity or hydrophilicity of the fibers seems one of the factors determining the stereoregularity of the grafted polymers of methacrylic acid and methyl methacrylate. The complete mechanism determining the stereoregularity of the grafted polymer needs further investigation.

We wish to thank Japan Atomic Energy Research Institute for financial assistance.

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Received August 8, 1971