Polymer Journal, Vol. 30, No. 9, pp 764—766 (1998)

SHORT COMMUNICATIONS

Radical Polymerization of Monovinyl Sebacate and Poly(vinyl alcohol) from Its Polymer

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(Received March 13, 1998)

KEY WORDS Monovinyl Sebacate / Vinyl Ester / Poly(vinyl alcohol) / Stereoregularity / Syndiotacticity / Solvent Effect /

Many studies and discussions on the syntheses and polymerizations of vinyl esters have been done from the viewpoint of the effective preparation of stereoregulated poly(vinyl alcohol) (PVA). The influence of chain length or bulkiness of acyl units in vinyl esters, and solvent effect in the course of polymerization on the stereoregularity of the resulting polymer have been reported.[1-6] A few reports can be found on the synthesis and polymerization of vinyl ester having a polar group in the acyl residual position,[7] and investigation on stereoregularity of PVA derived from such a vinyl ester has apparently not been published to date.

In the present work, monovinyl sebacate (9-vinyloxycarbonyl nonic acid) (MVS) with a polar terminal group in acyl residual position was newly synthesized, and its radical polymerization was attempted. To clarify the influence of the polar terminal group of vinyl ester on the stereoregularity of the resulting polymer, the polymerizations of vinyl decanoate (VD), which has the same number of carbon atoms in the acyl residual unit as MVS and has no polar terminal group, were carried out.

EXPERIMENTAL

Synthesis of MVS

Twenty-two grams sebacic acid were dissolved in 900 ml vinyl acetate under reflux, and then 0.44 g mercury(II) acetate was added to the solution. After stirring for 30 min, 0.04 ml of 100% sulfuric acid was added and refluxing was continued for more 6 h.

At the end of the reaction, the solution was neutralized with sodium acetate. After removal of unreacted vinyl acetate by vacuum distillation, the residue was dissolved in 5% aqueous sodium carbonate solution. Divinyl sebacate was removed from the solution by extraction with diethyl ether. By acidification of the solution, MVS and unreacted sebacic acid were deposited. They were dissolved in diethyl ether and separated from the aqueous phase. After removal of ether from ether fraction, *n*-hexane was added to the residue. The desired MVS and slight amount of sebacic acid were removed into the *n*-hexane phase. Further purification of the *n*-hexane fraction was carried out by silica gel column chromatography using *n*-hexane and ethyl acetate mixed solution (1 : 1, v/v) as the eluent. The isolated MVS was recrystallized from *n*-hexane and dried under vacuum. Powdery white MVS was obtained in 18% yield.

Polymerization

Two grams MVS (8.8 mmol), 8.5 mg of α,α'-azobisisobutyronitrile (AIBN, 0.052 mmol) and 20 ml of solvent were charged in a Kjeldahl flask. After the content was degassed by the freeze-thaw method, the flask was sealed under vacuum. Polymerizations were carried out at 20°C and 60°C with stirring. In the polymerization at 20°C, the content was irradiated with a high pressure mercury lamp. After polymerization, the reactant was poured into *n*-hexane. Collected polymer (PMVS) was purified by reprecipitation and dried under vacuum. Polymerization of VD was carried out in a similar manner as for MVS.

Saponification

Ten milliliters 25% KOH–methanol solution were dropped slowly into 100 ml of 1% tetrahydrofuran (THF) solution of PMVS with stirring. Saponification was carried out at 60°C for 20 min under a nitrogen atmosphere. The saponified polymers were filtered, washed with methanol, and dried under vacuum.

Measurements

^{1}H NMR spectrum was recorded on a JEOL JNM EX270 at 60°C using dimethyl sulfoxide (DMSO)-d_6 as solvent. Tacticity of PVA was determined by evaluating the triplet spectrum of hydroxyl proton in a tactic structure.[8]

Mass spectrum was obtained under fast atom bombardment at 6 keV using JEOL MStation JMS-700. Elemental analysis was performed on a Yanaco CHN corder MT-5. GPC was performed on a Tosoh GPC system with a RI detector and Waters Ultra Styragel Plus MX columns. THF was used as the eluent and standard polystyrene samples were used for calibration.

RESULTS AND DISCUSSION

Monovinyl Sebacate (MVS)

MVS was prepared by the transesterification reaction

of vinyl acetate with sebacic acid. Contents of carbon and hydrogen atoms of the product determined by the elemental analysis were 62.9% (calcd; 63.1%) and 8.85% (calcd; 8.83%), respectively.

Main fragment ion peaks confirmed on the mass spectrum of the product were $[MH]^+$ (*m/z* 229, relative intensity 9.8), $[MNa]^+$ (251, 100), $[M-OH]^+$ (211, 16.8), and $[M-(OCH=CH_2)]^+$ (185, 48.3). The ^1H NMR spectrum satisfied the structure of MVS (Figure 1). These data support that this substance is MVS. Purified MVS was white powdery crystals, and melted at 35°C. It could be dissolved in acetone, hexane, methanol, benzene, ethyl acetate, diethyl ether, and chloroform.

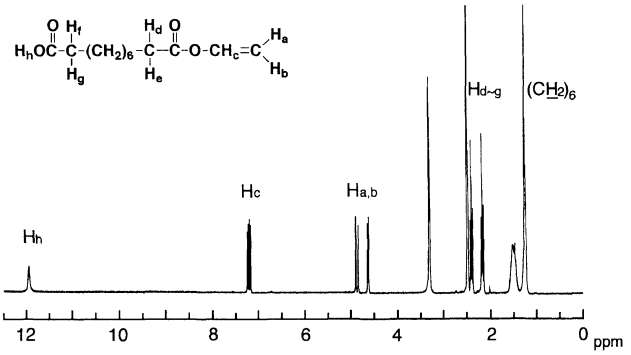

Figure 1. ^1H NMR spectrum of MVS.

Radical Polymerization of MVS, and Stereoregularity of PVA Derived from the Resulting PMVS

The results of radical polymerizations of MVS at 20°C and 60°C are listed in Table I. MVS was found to have a radical polymerizability, and PMVS with weight-average molecular weight of *ca.* 94000 was obtained by the polymerization at 20°C when using *n*-hexane as a

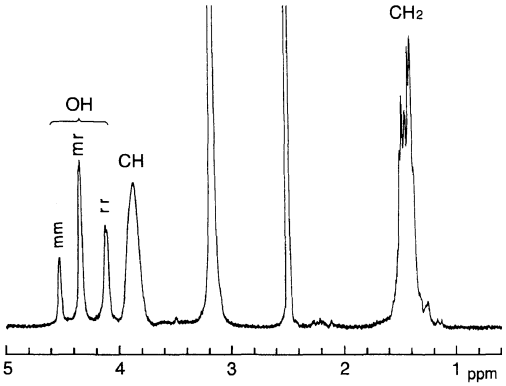

Figure 2. ^1H NMR spectrum of PVA from PMVS obtained by polymerization in *n*-hexane at 20°C.

Table I. Data for radical polymerization of MVS[a]

Polymerization temp/°C	Solvent	Polymerization time/h	Conversion %	M_w[b] ($\times 10^{-3}$)	M_n[b] ($\times 10^{-3}$)
20[c]	*n*-Hexane	120	68.2	94.4	16.6
	Methanol	120	81.0	30.6	9.8
	DMSO	89	38.3	45.9	13.8
60	Methanol	70	37.0	18.2	9.1

[a] Monomer : Solvent = 1 : 10 (w/v); [AIBN], 0.6 mol% for monomer. [b] Weight-average molecular weight (M_w) and number-average molecular weight (M_n) determined by GPC. [c] Irradiated with a high pressure mercury lamp.

Table IIa. Tacticities of PVA from PMVS

Polymerization temp/°C	Solvent in polymerization	Triad[a]/%			Diad[a]/%	
		I	*H*	*S*	*i*	*s*
20	*n*-Hexane	10.9	50.2	38.9	36.0	64.0
	Methanol	15.4	48.6	36.0	39.7	60.3
	DMSO	20.1	51.4	28.5	45.8	54.2
60	Methanol	15.4	49.3	35.3	40.1	59.9

[a] Determined from ^1H NMR spectrum: *i*, *I*, isotacticity; *H*, heterotacticity; *s*, *S*, syndiotacticity.

Table IIb. Tacticities of PVA from PVD

Polymerization temp/°C	Solvent in polymerization	Triad[a]/%			Diad[a]/%	
		I	*H*	*S*	*i*	*s*
20	*n*-Hexane	17.6	48.0	34.4	41.6	58.4
	Methanol	15.8	49.9	34.3	40.7	59.3
	DMSO	18.2	51.4	30.4	43.9	56.1
60	Methanol	17.4	48.6	33.9	41.8	58.2

[a] Determined from ^1H NMR spectrum: *i*, *I*, isotacticity; *H*, heterotacticity; *s*, *S*, syndiotacticity.

solvent.

PVA having a degree of saponification above 99.8% was derived from the PMVS. ^{1}H NMR spectrum of the PVA is shown in Figure 2, and tacticities determined from the spectrum are listed in Table IIa. Table IIb shows the tacticities of PVAs derived from poly(vinyl decanoate)s (PVD) polymerized under the same conditions as PMVS.

The syndiotacticity of PVA derived from PMVS obtained by polymerization in methanol at 20°C is 60% (diad), and that from PMVS polymerized in *n*-hexane is 64%. PVA from PMVS shows higher syndiotacticity than commercially available PVA (*ca.* 54% diad) obtained by saponification of poly(vinyl acetate) (PVAc),[9] possibly due to the greater steric effect of the acyl residual group of MVS than that of vinyl acetate.

The replacement of acyl residual unit of vinyl ester by bulky group, *e.g.*, trimethyl or phenyl group increases the syndiotacticity of the polymer owing to the steric hindrance.[1,10] The elongation of methylene sequences of acyl residual side groups of vinyl ester affects to a lesser extent the stereoregularity of the polymer.[11] The syndiotacticity of PMVS is higher than that of PVAc or PVD (Table IIb), except for the polymers prepared in DMSO, and the syndiotacticity of PVD is little affected by differences in solvent used in the present work, while that of PMVS is remarkably affected. These results clearly demonstrate the influence of terminal carboxyl group in MVS acyl residual unit on the stereoregularity of PMVS.

We assume that there should be contribution of appreciable intra- and inter-molecular interaction formed by terminal carboxyl group of MVS upon increase in syndiotacticity of PMVS. If there is some possibility of intra-molecular cyclization caused by hydrogen bonding the terminal carboxyl group with ester carbonyl group at the site of acyl residual position, the formed quasi cyclic structure should increase steric effect on MVS skeletals. A non-polar solvent may promote the steric effect. Further investigation must be done to make clear the inherent effects of the terminal carboxyl groups of MVS on the stereoregularity of PMVS.

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