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Short communication

Radical polymerization behavior of vinyl phenylsufonylacetate

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Abstract

Vinyl phenylsulfonylacetate (VPSA) was prepared by the reaction of vinyl chloroacetate with sodium benzenesulfinate in acetone in the presence of a phase-transfer catalyst. VPSA showed a high radical homopolymerizability similar to vinyl acetate in spite of the fact that VPSA carries a phenyl group. The polymerization of VPSA with 2,2′-azobisisobutyrate (MAIB) was kinetically investigated in acetone. The overall activation energy of the polymerization was 27.6 kcal/mol. The polymerization rate (R_p) at 50 °C was expressed by $R_p = k[\text{MAIB}]^{0.67}[\text{VPSA}]^{1.1}$. Poly(VPSA) showed exothermic (27 °C) and endothermic (57 °C) peaks in its DCS curve, corresponding to crystallization and melting. The tacticity of poly(VPSA) was estimated to be rr = 29, mr = 49, and mm = 22.

Keywords: Radical polymerization; Kinetic study; Vinyl ester; Tacticity; Poly(vinyl alcohol)

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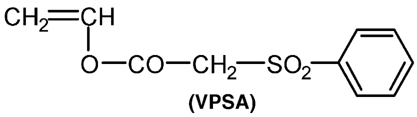
1. Introduction

Previously we reported that the radical polymerization of 2-thiocyanatoethyl vinyl ether (TCEVE) proceeded almost exclusively with intramolecular transfer of the cyano group (radical group-transfer polymerization) to yield a polymer containing ether and thioether linkages in the main chain [1]. On the other hand, the radical polymerization of vinyl thiocyanatoacetate (VTCA) as an ester analogue of TCEVE proceeded through normal vinyl addition and intramolecular transfer of the cyano group, where the cyano group transfer became progressively more important with decreasing monomer concentration [2].

1,5-Phenyl migrations are well known to occur on suitable low molecular-weighted radicals through six-membered cyclic intermediates with a hexadienyl radical [3,4]. Homolytic ipso substitution of phenylsulfonyl group on the benzene ring is also described [5]. Therefore, we have prepared and examined the radical polymerization behavior of vinyl phenylsulfonylacetate (VPSA) as another vinyl ester candidate for the radical group-transfer polymerization. The tacticity of the resulting poly(VPSA) was also estimated using poly(vinylalcohol) (PVA) derived from poly(VPSA). This article describes the results of kinetic study of radical polymerization of VPSA and characterization of the resulting polymer.


(VPSA)

2. Experimental

VPSA was prepared by the reaction of vinyl chloroacetate with sodium benzenesulfinate at room temperature in acetone for 15 h in the presence of

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tetra-*n*-butylammonium bromide as a phase-transfer catalyst. The crude VPSA was purified by chromatography where a silica gel column and an ethyl acetate/*n*-hexane [3:2(v/v)] mixture as developing solvent were used. Purified VPSA was identified by ^{1}H- and ^{13}C-NMR spectroscopy (JEOL EX-400 spectrometer; 400 MHz for ^{1}H and 100 MHz for ^{13}C) and elemental analysis. Dimethyl 2,2′-azobisisobutyrate (MAIB) was recrystallized from methanol. Di-*t*-butyl peroxide (DBPO) was used after distillation. Tri-*n*-butylborane solution in tetrahydrofuran (THF) was used as received. Solvents were used after distillation.

Polymerizations were conducted in degassed and sealed glass tubes at a given temperature with shaking. The resulting poly(VPSA) was isolated by pouring the polymerization mixture into a large excess of methanol. The number-average (M_n) and weight-average (M_w) molecular weights of the polymer were determined by gel permeation chromatography (GPC) (TOSO HLC-802 chromatograph) with calibration with poly(styrene) standards. For a kinetic study, the polymerization of VPSA was also conducted in a degassed and sealed Pyrex tube (5 mm diameter) in a custom-made aluminum furnace, in which FT-near infrared spectroscopic measurements were performed with a JASCO INT-400 spectrometer equipped with a MCT (mercury cadmium tellurium) detector [6,7]. The conversion of VPSA was monitored in situ by the absorbance at 6200 cm^{-1}as the overtone absorption due to the =C–H stretching vibration. Dynamic thermogravimetry (TG) of the polymer was performed under a nitrogen atmosphere (flow rate = 20 ml/min) with a Shimadzu TDA-50 thermogravimeter at a heating rate of 10 °C/min. Differential scanning calorimetric (DSC) curve was obtained at a heating rate of 10 °C/min (Shimadzu DSC-50).

Poly(VPSA) was hydrolyzed to PVA as follows; 20 ml of a methanol solution of KOH (2 g) was added dropwise at 40 °C to 200 ml of a THF solution of poly(VPSA) (1 g). The precipitated PVA was filtered, washed many times with methanol, and dried. Its tacticity was analyzed by ^{13}C-NMR.

3. Results and discussion

The polymerization of VPSA with MAIB at 50 °C in acetone was compared that of vinyl acetate (VAc), where the concentrations of the monomers and MAIB were 0.73 and 5.00×10^{-2} mol/l. Nearly same time-conversion curves were observed for both the monomers. The resulting poly(VPSA) and poly(VAc) showed comparable degrees of the polymerization (40 for poly-(VPSA) and 64 for poly(VAc) by GPC) and the same polydispersities (1.6). VAc is well known to exhibit much lower homopolymerizability in benzene than in non-aromatic solvents such as ethyl acetate, and much higher homopolymerizability than vinyl benzoate. These facts are explained by interaction of propagating poly(vinyl ester) radicals with the benzene rings [8–11]. Therefore, the similar homopolymerizabilities here observed for VPSA and VAc are noteworthy. The strongly electron-accepting character of the phenylsulfonyl group might enhance the radical homopolymerizability of VPSA. The poly(VPSA) was soluble in acetone, chloroform, THF, dimethyl sulfoxide, and *N*,*N*-dimethylformamide, and was insoluble in acetonitrile, methyl ethyl ketone, *n*-hexane, toluene, methanol, and water.

The polymerization of VPSA with MAIB was kinetically investigated in acetone. Fig. 1 presents time-conversion curves observed in the polymerization at different temperatures where the concentrations of VPSA and MAIB were 0.73 and 5.00×10^{-2} mol/l, respectively. From the Arrhenius plot of the polymerization rate (R_p) estimated from the time-conversion curve at each temperature, the overall activation energy of the polymerization was calculated to be 27.6 kcal/mol. This value was similar to that (26.8 kcal/mol) for the polymerization of VTCA with MAIB in acetone [2].

R_p was estimated at 50 °C when the MAIB concentration was changed at a fixed VPSA concentration of 0.73 mol/l. R_p was proportional to the 0.67th power of the initiator concentration. The effect of the monomer concentration on R_p was also examined at 50 °C, where the VPSA concentration was varied fixing the MAIB concentration at 5.00×10^{-2} mol/l. R_p was found to increase in proportion to the 1.1th order of the monomer concentration. Thus the polymerization rate at 50 °C in acetone was expressed by $R_p = k[\mathrm{MAIB}]^{0.67}[\mathrm{VPSA}]^{1.1}$.

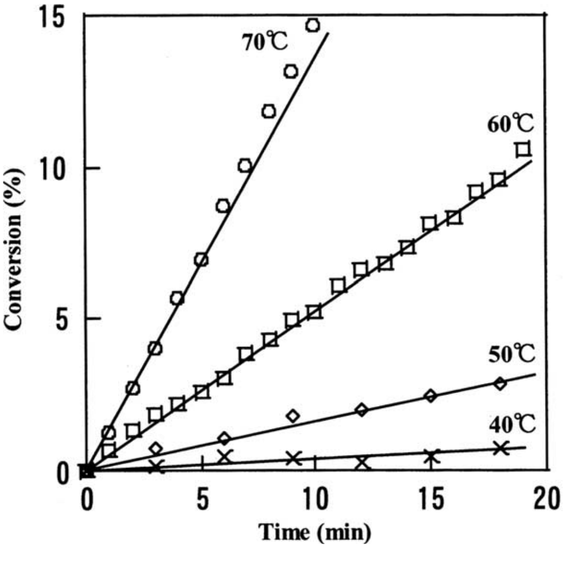


Fig. 1. Time-conversion curves in the polymerization of VPSA with MAIB at different temperatures in acetone: [VPSA] = 0.73 mol/l, [MAIB] = 5.00×10^{-2} mol/l.

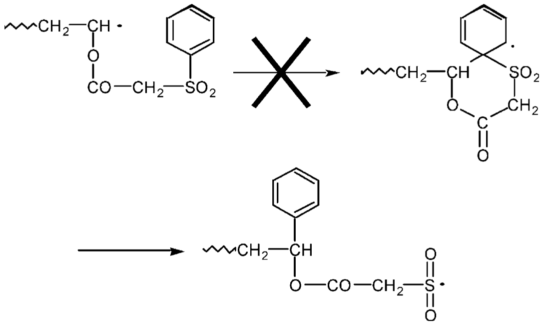
Table 1
Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(VPSA)s obtained in the polymerization of VPSA with MAIB in acetone

Temperature (°C)	[VPSA] (mol/l)	[MAIB]$\times 10^2$ (mol/l)	$M_n \times 10^{-3}$	M_w/M_n
40	0.73	5.00	9.21	1.53
50	0.73	5.00	9.07	1.59
60	0.73	5.00	8.25	1.53
70	0.73	5.00	7.57	1.52
50	0.73	1.00	9.84	1.57
50	0.73	2.50	9.47	1.56
50	0.73	7.50	9.44	1.59
50	0.73	10.0	9.64	1.55
50	0.30	5.00	6.11	1.33
50	0.50	5.00	7.76	1.45
50	1.00	5.00	11.3	1.68
50	1.50	5.00	15.6	1.81

This rate equation is similar to that of the usual radical polymerization involving bimolecular termination although the order with respect to the initiator concentration is somewhat higher than 0.5th.

Table 1 summarizes molecular weights (M_n) and molecular weight distributions (M_w/M_n) of poly(VPSA)s formed under various conditions. Similar to the usual radical polymerization, the molecular weight decreased with increasing temperature and decreasing monomer concentration. On the other hand, it was almost independent of the initiator concentration, suggesting a chain transfer reaction of the propagating polymer radical to acetone as solvent. The M_w/M_n value tended to increase with increasing monomer concentration.

^{1}H- and ^{13}C-NMR spectra of the resulting poly(VPSA) obtained at 50 °C in acetone revealed that the polymer was formed through conventional vinyl polymerization of VPSA. Use of different solvents (benzene, ethyl acetate, and methyl benzoate), temperatures (130 and 180 °C), and monomer concentrations (1.13 and 0.37 mol/l) did not cause any change in the polymer structure as analyzed by ^{1}H- and ^{13}C-NMR. These findings excluded our early expectation that VPSA polymerizes via phenyl group migration (Eq. (1)).



(1)

Thermal behavior of poly(VPSA) formed at 130 °C was analyzed by TG and DSC. The thermal degradation of the polymer began at 240 °C and exhibited a maximal rate at 300 °C. The residue at 500 °C was 10% of the initial polymer weight. In the DCS curve, an exothermic peak was observed at 27 °C and an endothermic one at 57 °C, probably corresponding to crystallization and melting.

The tacticities of poly(VPSA)s were estimated from the absorptions (64–69 ppm) due to the carbon attached to the OH group in the ^{13}C-NMR spectrum of PVAs derived from their hydrolysis. Table 2 summarizes the

Table 2
Tacticities of poly(VPSA)s formed under different conditions

Monomer	Solvent	Temperature (°C)	Tacticity (%)			Ref.
			mm	mr	rr	
VPSA	Bulk	60	22	49	29	This work
VPSA	Methanol	60	22	50	28	This work
VPSA	Acetone	50	26	50	24	This work
VPSA	Methyl benzoate	50	26	49	25	This work
VPSA	Methyl benzoate	130	26	49	25	This work
VPSA	Toluene	−40	25	49	26	This work
VAc	Toluene	40	22	49	29	[12]
VPi	Toluene	40	14	49	37	[12]

results of poly(VPSA)s formed under different conditions together with those for VAc and vinyl pivalate (VPi) [12]. Thus, the tacticities of poly(VPSA) were insensitive to the solvents and temperatures here used for the polymerization, although considerable effects of the solvent and temperature were observed on the tacticities of polymers in the polymerizations of some vinyl esters such as VAc and Vpi [13–16]. The tacticities of poly(VPSA)s were closely similar to those of the radical polymer of VAc [12].

Acknowledgements

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