NOTES

Stereochemistry of Free-Radical Polymerization of Bulky Vinyl Esters

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Poly(vinyl alcohol) (PVA) is produced by hydrolysis (saponification) of poly(vinyl ester)s obtained by free-radical polymerization and is used for various applications. The properties of PVA are dependent on stereochemical structure of the main chain and higher syndiotacticity generally gives better physical properties.[1] Syndiotactic specificity of vinyl ester polymerization is affected by the structure of vinyl ester monomers: vinyl pivalate (VPi) leads to higher syndiotactic specificity compared with vinyl acetate (VAc).[2-5] The higher syndiotactic specificity of VPi polymerization is considered to be based on steric repulsion of the bulky t-butyl group in the side chain of the monomer. In the present study, vinyl diphenylacetate (VDPAc) and vinyl triphenylacetate (VTPAc), which are bulkier than VPi, were prepared and stereochemistry of free-radical polymerization was investigated. Copolymerization of the bulky monomers with VAc or VPi was also carried out.

VAc   VPi   VDPAc   VTPAc
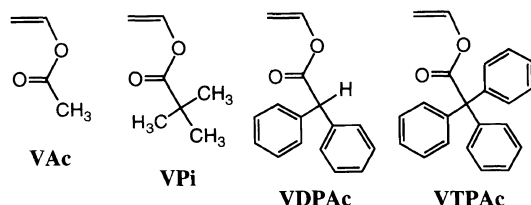
EXPERIMENTAL

Materials

VAc and VPi were washed with aqNaOH(2%) and distilled. α,α'-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were recrystallized from methanol. Diisopropyl peroxydicarbonate ((iso-PrOCOO)$_2$) was kindly provided by NOF Co. (Taketoyo-cho, Chita-gun, Aichi 470-23, Japan) and used as toluene solution (0.309 M). N,N-Dimethylaniline (DMA) was purified by distillation. The other reagents were purified by usual methods.

Synthesis of VDPAc[6]

VDPAc was synthesized by a published method[6] with modifications. In a 500-ml flask, diphenylacetic acid (20 g, 0.094 mol) was dissolved in vinyl acetate (110 ml, 1.19 mol) and HgSO$_4$ (5.6 g, 0.019 mol) was added to the solution. After stirring the mixture for 3.5 h at 80°C, the solid part was removed by filtration. The products were extracted with CHCl$_3$–aq Na$_2$CO$_3$. Removal of solvent

from the organic layer after dying on Na$_2$SO$_4$ gave crude products which were purified by distillation under reduced pressure. Yield 8.37 g (37%). bp 128—135°C/0.15 mmHg. ^{1}H NMR (400 MHz, CDCl$_3$, Me$_4$Si) δ 7.25—7.4 (m, 11H, aromatic H and vinyl –CH–), 5.10 (s, 1H, –CH–), 4.40 and 4.90 (d, 2H, vinyl –CH$_2$–).

Synthesis of VTPAc

VTPAc was synthesized by a published method[7] with modifications. In 500-ml flask, Hg(CH$_3$CO$_2$)$_2$ (11 g, 0.035 mol) was dissolved in distilled water (210 ml). Vinyl acetate (3.2 ml, 0.035 mol) and KCl (2.6 g, 0.035 mol) were added to the solution and the mixture was stirred for 24 h at ambient temperature. Water-insoluble product (ClHgCH$_2$CHO[8]) was collected with a centrifuge and dried under vacuum. Yield 6.4 g (66%). Triphenylacetyl chloride (8.2 g, 0.027 mol) prepared from the corresponding acid and SOCl$_2$ and ClHgCH$_2$CHO (9.7 g, 0.035 mol) were placed in a 500-ml flask equipped with a condenser under nitrogen atmosphere. Dry benzene (180 ml) was introduced and the mixture was refluxed with stirring for 14 h. Benzene was removed to give crude products after insoluble components were filtered off. The crude monomer was recrystallized from ether to give colorless crystals. Yield 3.9 g (47%). mp 114—115°C. ^{1}H NMR (400 MHz, CDCl$_3$, Me$_4$Si) δ 7.2—7.6 (m, 16H, aromatic H and vinyl –CH–), 4.60 and 4.80 (d, 2H, vinyl –CH$_2$–).

Polymerization and Saponification of Polymers

Polymerization was carried out under nitrogen atmosphere in a glass ampoule equipped with a three-way stop cock. The obtained polymers were converted to PVA by refluxing in a solution of NaOH (2 wt%) in a mixture of tetrahydrofuran (THF) and methanol.[9] PVA was purified by precipitation in methanol and dried under vacuum. The triad tacticity of PVA was determined based on –OH signals in ^{1}H NMR spectra taken in dimethylsulfoxide-d_6.[10]

Measurement

^{1}H NMR spectra were taken on a Varian Gemini 2000 spectrometer (400 MHz for ^{1}H measurement). GPC was performed with a Shodex System-21 GPC system equipped with a Shodex RI-71S detector using Shodex KF-803 and KF-806F columns connected in series (eluent, THF; flow rate, 1.0 ml min^{-1}; temp, 40°C).

RESULTS AND DISCUSSION

Homopolymerization of VDPAc and VTPAc

The conditions and results of polymerization of VDPAc and VTPAc in toluene at 40°C are shown in Table I along with those for VAc and VPi. Under the used conditions, VDPAc gave a polymer with a higher syndiotacticity (triad rr 42%, diad r 65%) than VPi and VAc. Although VDPAc has been reported not to give a high polymer,[6] in the present study we were able to obtain the polymers whose molecular weight was high enough for tacticity analysis as PVA. VTPAc gave only oligomeric products. This monomer may be too bulky to be polymerized.[7]

For the synthesis of poly(VDPAc) with higher syndiotacticity, various reaction conditions were applied to the polymerization (Table II). From the results of polymerization at different temperatures (runs 1—5), a higher polymerization temperature was found to lead to a higher syndiotacticity. This temperature-tacticity relation is opposite to that observed for VPi polymerization in which a lower reaction temperature gives a higher syndiotactic specificity.[11,1b] Based on the Fordham plot[12] of the tacticity data of runs 1—5 (Figure 1), the difference of activation enthalpy and that of activation entropy between isotactic and syndiotactic propagations were determined to be $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger} = -408\,\text{cal mol}^{-1}$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger} = -2.5\,\text{cal deg}^{-1}\text{mol}^{-1}$, respectively, according to eq[12] 1:

$$\ln(P_i/P_s) = (\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})/R - (\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})/RT \quad (1)$$

where P_i and P_s are diad tacticity, R is gas constant $(1.987\,\text{cal deg}^{-1}\,\text{mol}^{-1})$, and T is polymerization temperature in K. Growing species in the VDPAc polymerization system may take a conformation leading to syndiotactic monomer addition for sterical reasons. Such conformation may be favored at a higher polymerization temperature resulting in higher syndiotactic specificity of polymerization. This assumption is supported by $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ obtained from Fordham plots.

Stereochemistry of the polymerization was also affected by solvent (runs 4, 6—9): alcoholic solvents gave higher syndiotacticities compared with hydrocarbon solvents. Monomer concentration slightly affected the stereochemistry of polymerization in methanol (runs 7 and 8). The polymerization in 2-propanol (run 9) gave the highest syndiotacticity in the present study (triad rr 46%, diad r 67.5%). Recently, PVA with a diad syndiotacticity of 69% was synthesized through polymerization of VPi in hexane at $-40°C$.[13] Although the poly(VDPAc) prepared in the present study has a slightly lower syndiotacticity, our polymerization may be advantageous considering, as far as stereochemical control is concerned, that the syndiotactic specific VDPAc polymerization does not require extremely low reaction temperature.

Copolymerization

Copolymerizations of VDPAc with VAc and VPi were carried out and tacticity of the obtained copolymers was

Table I. Polymerization of vinyl esters using $(\text{iso-PrOCO}_2)_2$ in toluene at 40°C[a]

Run	Monomer	[Monomer]$_0$ M	Yield[b] %	M_n[c] $\times 10^3$	M_w/M_n[c]	Tacticity[d] mm/mr/rr
1	VAc	7.51	85	6.1	2.22	22/49/29
2	VPi	5.27	81	13.2	2.27	14/49/37
3	VDPAc	3.97	25	6.9	1.60	12/46/42
4[e]	VTPAc	0.86	18[f]	1.0[g]		

[a] [Monomer]/[initiator] = 50. Time 24 h. [b] Polymer was isolated by precipitation in hexane (runs 1 and 3) or by removing volatile components under high vacuum (run 2). [c] Estimated by GPC using standard polystyrenes. [d] Estimated by ¹H NMR analysis in dimethylsulfoxide-d_6 of PVA derived from the original polymer. [e] In a mixture of tetrahydrofuran and toluene (20 : 1, vol/vol). [f] Estimated by ¹H NMR analysis of crude sample (CDCl_3). [g] Peak-top M_n value.
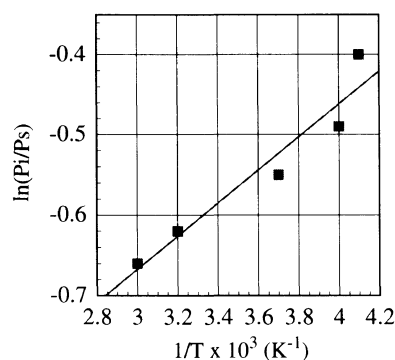

Figure 1. Fordham plots of the data of runs 1—5 in Table II.

Table II. Polymerization of VDPAc under various conditions[a]

Run	Initiator	Solvent	Temp °C	[Monomer]$_0$ M	Yield[b] %	M_n[c] $\times 10^3$	M_w/M_n[c]	Tacticity[d] mm/mr/rr
1	BPO	None	−30	3.86	22	4.6	1.45	16/48/36
2	BPO	None	−20	4.51	14	9.2	1.60	14/48/38
3	BPO-DMA[e]	None	0	4.37	24	9.4	1.72	13/47/40
4[f]	$(\text{iso-PrOCO}_2)_2$	Toluene	40	3.97	25	6.9	1.60	12/46/42
5	AIBN	None	60	4.31	27	6.9	1.50	12/44/44
6	$(\text{iso-PrOCO}_2)_2$	Hexane	40	2.37	50	5.1	1.56	14/44/42
7	$(\text{iso-PrOCO}_2)_2$	MeOH	40	3.42	57	4.5	1.56	13/43/44
8	$(\text{iso-PrOCO}_2)_2$	MeOH	40	2.37	40	3.7	1.63	13/41/46
9	$(\text{iso-PrOCO}_2)_2$	2-Propanol	40	2.85	58	4.5	1.61	11/43/46

[a] [initiator]$_0$ = 0.079—1.50 M. Time 4 h (run 1), 1 h (run 2), 24 h (runs 3, 4, 7, 9), 70 h (run 5), 48 h (runs 6, 8). [b] Polymer was isolated by precipitation in hexane. [c] Estimated by GPC using standard polystyrenes. [d] Estimated by ¹H NMR analysis in dimethylsulfoxide-d_6 of PVA derived from the original polymer. [e] [BPO]$_0$/[DMA]$_0$ = 1. [f] Run 3 in Table I.

Table III. Copolymerization of VDPAc (M_1) with VAc or VPi (M_2) using (iso-$PrOCO_2$)$_2$ in toluene at 40°C[a]

Run	M_2	M_1/M_2 in feed	Yield[b] %	M_1/M_2 in remaining monomer	M_n[c] $\times 10^3$	M_w/M_n[c]	Tacticity[d] mm/mr/rr
1	VAc	90/10	25	89/11	7.0	1.58	15/45/40
2	VAc	49/51	32	47/53	7.4	1.62	17/47/36
3	VAc	30/70	46	28/72	8.2	1.75	17/49/34
4	VAc	10/90	69	8/92	9.3	1.94	20/48/32
5	VPi	80/20	20	81/19	7.6	1.65	14/47/39
6	VPi	50/50	29	52/48	8.8	1.71	15/49/36
7	VPi	20/80	41[e]	22/78	11.8	1.85	15/49/36

[a] [Monomer]$_0$ = 3.97—7.51 M. [Initiator]$_0$ = 0.079—0.15 M. Time 24 h. See runs 1—3 in Table I for the results of homopolymerization of M_1 or M_2. [b] Polymer was isolated by precipitation in hexane. [c] Estimated by GPC using standard polystyrenes. [d] Estimated by ^{1}H NMR analysis in dimethylsulfoxide-d_6 of PVA derived from the original polymer. [e] Polymer was isolated by precipitation in MeOH–H_2O (1 : 1, vol/vol).

investigated (Table III). The compositions (M_1/M_2) of remaining monomers were quite similar to those of fed monomers even at the rather high polymer yield, suggesting monomer reactivity ratios of $r_1 \approx r_2 \approx 1$ for the both copolymerizations. As for the stereochemistry of copolymerization, syndiotacticity of the obtained copolymers decreased with an increase in the content of VAc or VPi unit in the polymer chain and no particular improvement in stereospecificity was observed by the copolymerization. Copolymerization of VTPAc with VAc was also performed but only oligomeric products were obtained.

CONCLUSION

Free-radial polymerization of VDPAc exhibits higher syndiotactic specificity than polymerization of VPi.

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