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NOTES

Asymmetric Anionic Polymerization of *N*-3-Hydroxyphenyl-*N*-phenylacrylamide Derivatives

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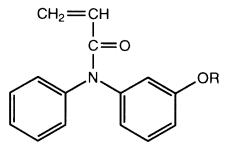
It has been known that *N,N*-diphenylacrylamide (DPAA) gives an optically active polymer in the polymerization initiated with chiral anionic initiators.[1,2] However, the detailed structure of the obtained polymer including tacticity had not been clarified. Recently, we found a method of transforming poly(DPAA) into poly(methyl acrylate) (PMA) which allowed us to estimate the tacticity of poly(DPAA) by ^{1}H NMR method.[3] We also reported that *meta*-substituted *N,N*-diphenylacrylamides afford optically active polymers with conformational chirality in asymmetric anionic polymerization, and the *meta*-substituents strongly affect the tacticity and optical activity of the obtained polymers.[4] Herein we report the asymmetric anionic polymerization of *N*-3-hydroxyphenyl-*N*-phenylacrylamide derivatives bearing a bulky substituent on the hydroxy group. Three novel monomers (3-RODPAA), *N*-(3-(*tert*-butyldimethylsilyloxy)phenyl)-*N*-phenylacrylamide (3-SiODPAA), *N*-phenyl-*N*-(3-pivaloyloxyphenyl)acrylamide (3-PvODPAA) and *N*-phenyl-*N*-(3-(2-phenylbutyryloxy)phenyl)acrylamide (3-PBODPAA) were synthesized and polymerized with the complex of fluorenyllithium and (−)-sparteine (FlLi-(−)-Sp). The effect of the bulky substituents on the polymerization and the chiroptical properties and tacticity of the obtained polymers was investigated.



R = $Si(CH_3)_2C(CH_3)_3$: 3-SiODPAA
$COC(CH_3)_3$: 3-PvODPAA
$COCH(Ph)CH_2CH_3$: 3-PBODPAA
CH_3 : 3-MeODPAA

EXPERIMENTAL

Measurements

^{1}H NMR spectra were obtained on a Varian Gemini-2000 (400 MHz) or UNITY-INOVA (500 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Infrared (IR) spectra were recorded on a JASCO FT/IR-7000 spectrometer. Specific rotation was measured on a JASCO DIP-181 polarimeter at 25°C. Circular dichroism (CD) and ultraviolet (UV) spectra were obtained with a JASCO J-720 and a JASCO Ubest-55 spectrophotometer, respectively. Mass spectra (FD-MS) were recorded with a JEOL JMS-AX505HA mass spectrometer. Gel permeation chromatographic (GPC) analysis was carried out on a JASCO BIP-1 chromatograph equipped with a refractive index detector (JASCO 830-RI) or on a JASCO PU-980 chromatograph equipped with a UV (JASCO UV-970) and a polarimetric (JASCO OR-990) detectors. Two columns (TSK G5000H and Shodex AC802.5) were connected in series and $CHCl_3$ was used as eluent. Caliblation was performed using standard polystyrene.

Materials

Toluene was purified in the usual manner, mixed with a small amount of butyllithium (*n*-BuLi), and distilled under high vacuum just before use. *n*-BuLi was synthesized from 1-chlorobutane and lithium powder in heptane. Fluorene (Fl) (Nacalai Tesque) was recrystallized from ethanol and hexane. (−)-Sparteine ((−)-Sp) (Sigma) was dried over calcium hydride and distilled under a reduced pressure. A radical initiator diisopropyl peroxydicarbonate ((*iso*-$PrOCO_2)_2$) was kindly provided from NOF Co. and used as a toluene solution. Other commercially available materials were used without further purification.

Three novel monomers were synthesized in benzene by treating acryloyl chloride with 3-hydroxydiphenylamine derivatives whose hydroxy group was protected with the corresponding bulky substituent in the presence of *N,N*-dimethylaniline. 3-PBODPAA was purified by recrystallization from ether and hexane. 3-SiODPAA and 3-PvODPAA were purified by column chromatography on silica gel (ether/hexane = 1/5), and then dried over calcium hydride as a toluene solution. The toluene solution was filtrated under an N_2 atmosphere just before polymerization.

3-SiODPAA: IR (neat) 1676, 1597, 1489, 1404, 1328, 1261, 785, 704 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.16 (s, 6H, $Si(CH_3)_2$), 0.95 (s, 9H, $C(CH_3)_3$), 5.62 (dd, 1H, J = 2.0, 10.5 Hz, vinyl), 6.20 (dd, 1H, J = 10.5, 17.0 Hz, vinyl), 6.46 (dd, 1H, J = 2.0, 17.0 Hz, vinyl), 6.7—7.4 (m, 9H, aromatic); MS (FD) m/z 353 (M^+).

3-PvODPAA: IR (neat) 1752, 1673, 1595, 1489, 1404, 1328, 1261, 1207, 1112, 702 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.33 (s, 9H, $C(CH_3)_3$), 5.65 (dd, 1H, J = 2.0, 10.0 Hz, vinyl), 6.19 (dd, 1H, J = 10.0, 16.5 Hz, vinyl), 6.48 (dd, 1H, J = 2.0, 16.5 Hz, vinyl), 6.9—7.5 (m, 9H, aromatic); MS (FD) m/z 323 (M^+).

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Table I. Radical and anionic polymerization of 3-RODPAA in toluene[a]

Entry	Monomer	Initiator	Yield[b] %	$\overline{DP}$[c]	$\bar{M}_w/\bar{M}_n$[c]	Tacticity[d] *m*:*r*
1	3-SiODPAA	(*iso*-$PrOCO_2)_2$	14[e]	96	2.26	29:71
2	3-PvODPAA	(*iso*-$PrOCO_2)_2$	60	88	1.23	20:80
3	3-PBODPAA	(*iso*-$PrOCO_2)_2$	67	79	1.25	35:65
4	3-MeODPAA	(*iso*-$PrOCO_2)_2$	81	102	1.37	29:71
5	3-SiODPAA	*n*-BuLi	0[e]	—	—	—
6	3-PvODPAA	*n*-BuLi	4[e]	72	1.41	74:26
7	3-PBODPAA	*n*-BuLi	0[e]	—	—	—
8	3-MeODPAA	*n*-BuLi	21[e]	136	1.44	86:14

[a] Radical polymerization: [Monomer]/[Initiator] = 50; temp = 40°C; time = 24 h; Anionic polymerization: [Monomer]/[Initiator] = 20; temp = −98°C; time = 2 h. [b] Hexane insoluble part. [c] Determined by GPC (polystyrene standard) using poly(methyl acrylate) derived from the original polymer. [d] Determined by ^{1}H NMR analysis using poly(methyl acrylate) derived from the original polymer. [e] Methanol insoluble part.

Table II. Polymerization of 3-RODPAA with FlLi-(−)-Sp in toluene[a]

Entry	Monomer	Temp °C	Yield[b] %	$\overline{DP}$[c]	$\bar{M}_w/\bar{M}_n$[c]	Tacticity[d] *m*:*r*	$[\alpha]_{365}^{25}$[e]
1	3-SiODPAA	−78	77	53	1.05	52:48	−48°
2	3-SiODPAA	−98	50	51	1.05	54:46	−69°
3	3-PvODPAA	−78	36	64	1.05	50:50	−41°
4	3-PvODPAA	−98	41	64	1.06	55:45	−36°
5	3-PBODPAA	−78	96	63	1.08	57:43	−51°
6	3-PBODPAA	−98	51	51	1.05	61:39	−101°
7	3-MeODPAA	−78	96	48	1.11	53:47	−116°
8	3-MeODPAA	−98	93	52	1.06	58:42	−130°

[a] [Monomer]/[Initiator] = 20; time = 2 h. [b] Methanol insoluble part. [c] Determined by GPC (polystyrene standard) using poly(methyl acrylate) derived from the original polymer. [d] Determined by ^{1}H NMR analysis using poly(methyl acrylate) derived from the original polymer. [e] Measured in $CHCl_3$ (c = 1.0).

3-PBODPAA: IR (KBr) 1752, 1671, 1487, 1402, 1332, 1257, 1209, 1141, 700 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.97 (t, 3H, J = 7.5 Hz, CH_3), 1.89 and 2.20 (m, 2H, CH_2), 3.66 (t, 1H, J = 7.5 Hz, CH), 5.63 (dd, 1H, J = 2.0, 10.5 Hz, vinyl), 6.17 (dd, 1H, J = 10.5, 16.5 Hz, vinyl), 6.46 (dd, 1H, J = 2.0, 16.5 Hz, vinyl), 6.8—7.5 (m, 14H, aromatic); *Anal.* Calcd for $C_{25}H_{23}NO_3$: C, 77.90%; H, 6.01%; N, 3.63%. Found: C, 77.83%; H, 6.04%; N, 3.59%.

Polymerization Procedure

Polymerization was carried out in a dry glass ampule equipped with a three-way stopcock under a dry N_2 atmosphere. The procedure was the same as our previous method.[4] The polymerization was initiated by adding an initiator solution to a monomer solution with a syringe. The polymerization was terminated with a small amount of methanol. Then the polymer was poured into a large amount of methanol, collected by centrifugation, and dried *in vacuo*.

The molecular weight and tacticity of the obtained polymers were determined by GPC and ^{1}H NMR analyses,[5] respectively, after the polymers had been carefully converted into poly(methyl acrylate) according to the method that we established for poly(DPAA).[3]

RESULTS AND DISCUSSION

Table I summarizes the results of the radical polymerization of 3-RODPAA with (*iso*-$PrOCO_2)_2$ at 40°C and the anionic polymerization with *n*-BuLi at −98°C. The polymerization results of 3-MeODPAA[4] (entry 4 and 8 in Table I) are also included for comparison. From the yield of polymer, the bulky substituents seem to reduce the polymerizability of the monomers. In the radical polymerization, the polymers rich in syndiotacticity (r = 65—80%) were obtained, and poly(3-PvODPAA) (entry 2) had the highest syndiotacticity. The substituents greatly influenced the solubility of the polymers. The radically obtained polymers except for poly(3-SiODPAA) were insoluble in hexane, but poly(3-SiODPAA) (entry 1) was soluble in hexane and therefore was collected as a methanol-insoluble part.

On the other hand, the anionic polymerization of 3-SiODPAA and 3-PBODPAA gave no polymer (entry 5,7), and 3-PvODPAA gave a polymer rich in isotacticity (m = 74%) in a very low yield (entry 6). The ^{1}H NMR analysis of the methanol-soluble part recovered in entry 6 suggested that a side reaction, 1,2-addition of the initiator (*n*-BuLi) to the acyloxy group of *meta*-substituent took place.

Table II shows the results of the asymmetric anionic polymerization of the four monomers with the complex of FlLi and (−)-Sp as an initiator. In contrast to the anionic polymerization with *n*-BuLi, the polymerization proceeded in good yields to afford the polymers slightly rich in isotacticity (m = 50—61%) with a narrow molecular-weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.05—1.11), and the all polymers were optically active showing negative specific rotation. The (−)-Sp coordinating to a Li cation and the bulkiness of fluorenyl group may depress

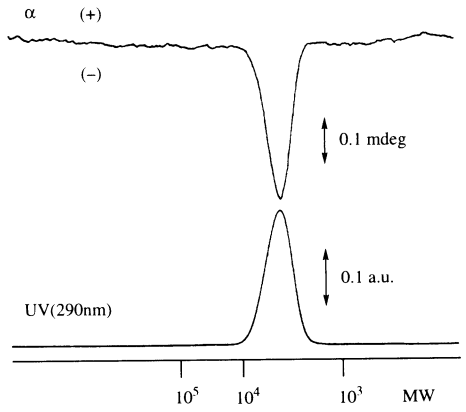


Figure 1. GPC curves of poly(3-PBODPAA) obtained with FlLi-(−)-Sp at −98°C (Table II, entry 6).

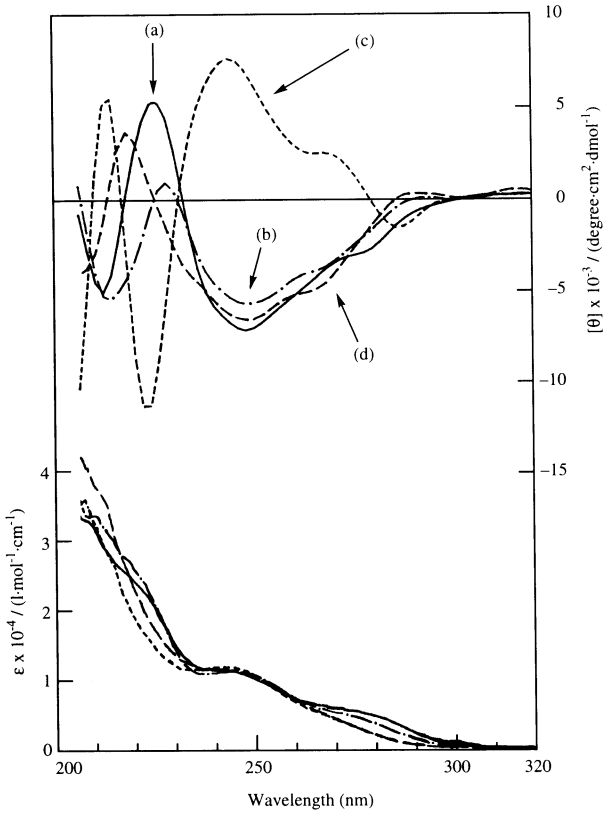
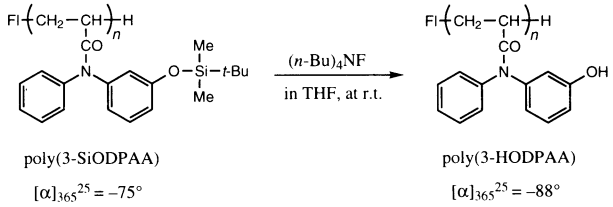


Figure 2. CD and UV spectra of poly(3-MeODPAA) (a), poly(3-SiODPAA) (b), poly(3-PvODPAA) (c), and poly(3-PBODPAA) (d) obtained with FlLi-(−)-Sp in toluene at −98°C (in THF).

the side reaction. The tacticity and specific rotation of the obtained polymers were affected by the substituent on phenyl group. In the polymerization of 3-PBODPAA, the polymer with the highest negative specific rotation ($[\alpha]_{365}^{25} = -101°$) and relatively high isotacticity (m = 61%) was obtained (entry 6). Since 3-PBODPAA is a chiral monomer, one can expect the possibility of enantiomer selection in the polymerization with the optically active initiator FlLi-(−)-Sp. However, the HPLC analysis of recovered monomer with a chiral column suggested the absence of enantioselection.[6]

The optically active polymers were analyzed by GPC and CD measurements. Figure 1 depicts the GPC curve of poly(3-PBODPAA) (entry 6 in Table II) monitored with UV and polarimetric detectors. The polarimetric



poly(3-SiODPAA)
$[\alpha]_{365}^{25} = -75°$

poly(3-HODPAA)
$[\alpha]_{365}^{25} = -88°$

Scheme 1.

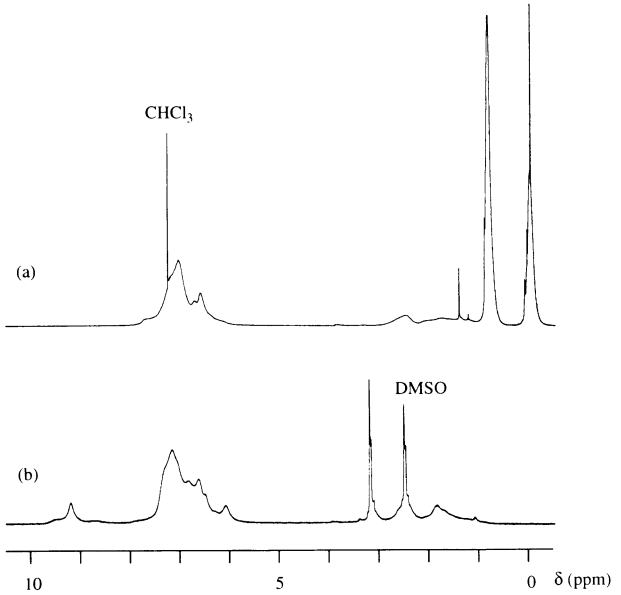


Figure 3. ^{1}H NMR spectra of poly(3-SiODPAA) (a), and poly(3-HODPAA) derived from desilylation of poly(3-SiODPAA) (b) ($CDCl_3$ for (a) and DMSO-d_6 for (b)).

detector demonstrated a negative peak whose pattern is quite similar to the UV curve. This suggests that the polymer is homogeneous with respect to structure and the optical activity of the polymer may be due to the prevailing one-handed helical conformation produced through the polymerization process.[2] Other polymers also provided analogous results in the GPC measurements.

The CD and UV spectra of poly(3-RODPAA) measured in tetrahydrofuran (THF) are shown in Figure 2. The broad CD peaks at 230—300 nm demonstrate that the phenyl groups of the polymers exist under chiral circumstances. Although poly(3-PvODPAA) showed negative optical rotation as well as other polymers, its CD pattern was opposite to those of other polymers. This suggests that poly(3-PvODPAA) may have opposite helicity to other polymers.

The effect of the substituents on optical rotation was also investigated by converting poly(3-SiODPAA) into poly(*N*-3-hydroxyphenyl-*N*-phenylacrylamide) (poly(3-HODPAA)). Desilylation reaction of poly(3-SiODPAA) was carried out with tetra-*n*-butylammonium fluoride (TBAF) in THF (Scheme 1).

The obtained poly(3-HODPAA) was insoluble in $CHCl_3$, but soluble in polar solvent such as THF and dimethylsulfoxide (DMSO). Figure 3 shows the ^{1}H NMR spectra of the original poly(3-SiODPAA) in $CDCl_3$ and the derived poly(3-HODPAA) in DMSO-d_6. After the desilylation, the peaks due to the *tert*-butyldimethylsilyl (TBDMS) group (δ −0.2—1.2 ppm) in Figure 3(a)

Table III. Analyses of poly(3-HODPAA) after desilylation of poly(3-SiODPAA)

Polymer	$\overline{DP}$[a]	$\bar{M}_w/\bar{M}_n$[a]	Tacticity[b] $m:r$	$[\alpha]_{365}^{25}$[c]	$[\phi]_{365}^{25}$[c]
3-HODPAA	48	1.04	54:46	−88°	−211°
3-SiODPAA	51	1.05	54:46	−75°	−268°

[a] Determined by GPC (polystyrene standard) using poly(methyl acrylate) derived from the original polymer. [b] Determined by ^{1}H NMR analysis using poly(methyl acrylate) derived from the original polymer. [c] Measured in THF ($c=0.1$).

completely disappeared and a peak due to the hydroxy group in Figure 3(b) appeared at δ 8.5—9.5. The optical rotation of poly(3-HODPAA) was measured in THF, and then transformed into poly(methyl acrylate) for GPC and ^{1}H NMR analyses. The results for poly(3-HODPAA) and the original poly(3-SiODPAA) are shown in Table III. Little difference was seen in the degree of polymerization (DP) and tacticity, suggesting that only desilylation proceeded during the reaction. Furthermore, the molar rotation ([ϕ]) of the polymers also showed little change, suggesting that the chiral conformation of the polymers was maintained even after the bulky TBDMS group was removed. The optically active polymer with a hydroxy group is interesting because one can readily convert the polymer to other chiral polymers by the treatment with optically active reagents such as (+)- and (−)-1-phenylethyl isocyanate.

In conclusion, the DPAA derivatives bearing bulky substituents on the *meta* position of phenyl group gave optically active polymers whose chirality must be due to a predominantly one-handed helical conformation. Poly(3-SiODPAA) was readily converted to poly(3-HODPAA) with a reactive hydroxy group. The polymer is expected to be useful to derive other chiral polymers.

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6. Complete resolution of (±)-3-PBODPAA was attained under the following conditions: Column, Chiralpak AD (Daicel); eluent, hexane/*iso*-propanol = 9/1; flow rate, 0.5 ml min^{-1}.