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Asymmetric Anionic Polymerization of Alkyl-Substituted *N,N*-Diphenylacrylamide Derivatives

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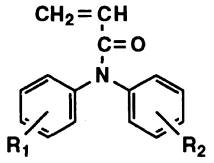
ABSTRACT: Five novel *N,N*-diphenylacrylamide derivatives bearing alkyl groups on a phenyl group were synthesized and polymerized with a chiral anionic initiator, the complex of (−)-sparteine and fluorenyllithium, in toluene at low temperature. Both position and size of the alkyl-substituents greatly affected the tacticity and optical activity of the polymer obtained. *N,N*-Di-4-tolylacrylamide gave a polymer possessing the highest isotacticity ($m=72\%$) and specific rotation ($[\alpha]^{25}_{365}=-423°$), which may be attributed to the chiral conformation of the main-chain. The asymmetric anionic polymerization of *N*-phenyl-*N*-(4-tolyl)acrylamide gave a chloroform-soluble polymer which was found to contain a polymer of high specific rotation ($[\alpha]^{25}_{365}=-1122°$) and isotacticity ($m=94\%$) through fractionation by GPC.

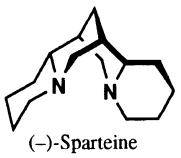
KEY WORDS Asymmetric Anionic Polymerization / Optically Active Polymer / *N,N*-Diphenylacrylamide / (−)-Sparteine / Tacticity / Helix /

Triphenylmethyl methacrylate (TrMA) is the first example of a vinyl monomer that directly affords an optically active, isotactic polymer ($[\alpha]_D=+334$—$383°$, $mm>99\%$) with one-handed helicity produced through the polymerization with a chiral anionic initiator.[1] The helical structure is maintained even in solution because of the steric repulsion between the bulky triphenylmethyl ester groups. *N,N*-Disubstituted acrylamides are known to give crystalline polymers by anionic polymerization,[2] and *N,N*-disubstituted acrylamides bearing bulky substituents such as *N,N*-diphenylacrylamide (DPAA) afford optical active polymers in the anionic polymerization with chiral initiators.[3,4] Recently, we reported a method of transformation of poly(DPAA) to poly(methyl acrylate) (poly(MA)), which allowed to determine the diad tacticity of poly(DPAA)s by ^{1}H NMR measurement.[5] We also reported the influence of Me, MeO, and Cl substituents introduced on the phenyl group of DPAA.[6]

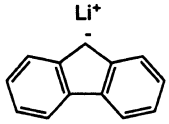
In the course of our study on the optically active poly(DPAA), inconvenience was found in solubility of the polymers obtained. The poly(DPAA) was not fully soluble in common organic solvents like chloroform or tetrahydrofuran (THF), while the above optically active polymers with *meta*-substituents were fully soluble in chloroform and THF. The introduction of a substituent at the meta position on the phenyl group improved solubility of the polymers. However, the optical activity and isotacticity of the polymer obtained were still much lower than those of the one-handed helical poly(TrMA).[1] Therefore, to enhance the stereoregularity and solubility of the polymer, we synthesized novel DPAA derivatives bearing various alkyl groups on the phenyl group. Herein, we report the asymmetric anionic polymerization of *N*-phenyl-*N*-(2-tolyl)acrylamide (2-MeDPAA), *N*-phenyl-*N*-(4-tolyl)acrylamide (4-MeDPAA), *N*-(4-hexylphenyl)-*N*-phenylacrylamide (4-HexDPAA), *N,N*-di-4-tolylacrylamide (4,4′-Me_2DPAA), and *N,N*-bis(4-butylphenyl)acrylamide (4,4′-Bu_2DPAA). The influence of the alkyl substituents on the optical activity and tacticity of the polymers obtained was mainly investigated.



Monomer		R_1	R_2
DPAA	=	H	H
2-MeDPAA	=	2-Methyl	H
4-MeDPAA	=	4-Methyl	H
4-HexDPAA	=	4-Hexyl	H
4,4′-Me_2DPAA	=	4-Methyl	4-Methyl
4,4′-Bu_2DPAA	=	4-Butyl	4-Butyl



(−)-Sparteine



Fluorenyllithium

EXPERIMENTAL

Measurements

^{1}H NMR spectra were recorded on a Varian VXR500S (500 MHz), a UNITY-INOVA (500 MHz) or a Gemini 2000 (400 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Optical rotation and circular dichroism (CD) spectra were measured on a JASCO DIP-181 polarimeter and a J-720L spectrometer, respectively. Ultraviolet (UV) and infrared (IR) spectra were recorded on a JASCO Ubest-55 and a FT-IR-7000 spectrometer, respectively. Mass spectra were recorded with a JEOL JMS-AX505HA mass spectrometer. Gel permeation chromatographic analysis (GPC) was performed on a JASCO 880-PU chromatograph equipped with a JASCO 875-UV ultraviolet detector (254 nm) and a Shodex OR-1 polarimetric detector (780 nm), or on a JASCO BIP-I chromatograph equipped with a JASCO 830-RI refractive index detector. Two commercial columns (TSK G5000H 60 × 0.72 (i.d.) cm, Shodex AC 802.5 50 × 0.72 (i.d.) cm) were connected in series, and chloroform was used as eluent. Calibration was performed using standard polystyrenes.

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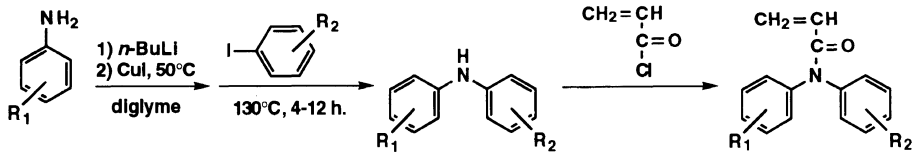


Scheme 1.

Monomer Synthesis

The monomers were synthesized from corresponding aniline derivatives in two steps as shown in Scheme 1.

Typical Procedure of N-Phenyl-4-Toluidine.[7] To a solution of 4-toluidine (50 g, 267 mmol) in diglyme (200 ml) was added *n*-butyllithium (*n*-BuLi, 1.65 M in hexane, 250 ml) dropwise at 0°C under nitrogen atmosphere. After hexane was evaporated under a reduced pressure, a suspension of copper(I) iodide (60 g, 315 mmol) in diglyme (100 ml) was added and the temperature was raised to 50°C. After 30 min, iodobenzene (60 ml, 536 mmol) was added, and stirring was continued for 5 h at 130°C. After the reaction mixture was cooled to room temperature, an excess of water was added to quench the reaction, and the resulting brown suspension was filtered through a celite plate to remove the precipitates. The filterate was extracted with hexane (300 ml × 3). The combined organic layers were dried over anhydrous sodium sulfate, and the solvents were evaporated under a reduced pressure. The crude product was first purified by distillation under a reduced pressure (bp = 84—130°C/0.3—0.4 mmHg), followed by recrystallization from hexane to afford *N*-phenyl-4-toluidine (54 g, 64% yield): mp = 79—83°C.

Synthesis of Diphenylacrylamides. The diphenylacrylamides were prepared by the reaction of acryloyl chloride (1.2 equiv.) with corresponding diphenylamine derivatives (1.0 equiv.) in dichloromethane in the presence of *N,N*-dimethylaniline (1.2 equiv.) the crude products were purified by flash chromatography on silica gel (eluent hexane/diethyl ether = 1/1) and by recrystallization several times from diethyl ether and then from hexane or cyclohexane.

N-Phenyl-N-(4-tolyl)acrylamide (*4-MeDPAA*). mp 75—76°C; IR (KBr) 1669, 1620, 1595, 1491, 1406, 1332, 1309, 1270 cm^{-1}; ^1H NMR (500 MHz) δ 2.35 (s, 3H, CH_3), 5.61 (dd, 1H, J = 2.0, 10.5 Hz, vinyl), 6.20 (dd, 1H, J = 10.5, 17.0 Hz, vinyl), 6.45 (dd, 1H, J = 2.0, 17.0 Hz, vinyl), 7.1—7.4 (m, 9H, aromatic). *Anal.* Calcd for $C_{16}H_{15}NO$: C, 80.99%; H, 6.37%; N, 5.90%. Found: C, 80.80%; H, 6.52%; N, 5.93%.

N-Phenyl-N-(2-tolyl)acrylamide (*2-MeDPAA*). mp 48—49°C; IR (KBr) 1661, 1620, 1493, 1404, 1323, 1263, 760 cm^{-1}; ^1H NMR (400 MHz) δ 2.11 (s, 3H, CH_3), 5.58 (d, 1H, J = 10.8 Hz, vinyl), 6.0—6.2 (br, 1H, vinyl), 6.45 (d, 1H, J = 16.8 Hz, vinyl), 7.1—7.4 (m, 9H, aromatic). *Anal.* Calcd for $C_{16}H_{15}NO$: C, 80.99%; H, 6.37%; N, 5.90%. Found: C, 80.99%; H, 6.42%; N, 5.91%.

N-(4-Hexylphenyl)-N-phenylacrylamide (*4-HexDPAA*). IR (neat) 1673, 1621, 1594, 1510, 1494, 1401, 1328, 1261 cm^{-1}; ^1H NMR (500 MHz) δ 0.88 (t, 3H, J = 7.0 Hz, CH_3), 1.2—1.4 (m, 6H, $CH_2CH_2CH_2$), 1.60 (m, 2H, CH_2), 2.59 (t, 2H, J = 8.0 Hz, CH_2), 5.62 (dd, 1H, J = 2.0, 10.0 Hz, vinyl), 6.20 (dd, 1H, J = 10.0, 17.0 Hz, vinyl), 6.46 (dd, 1H, J = 2.0, 17.0 Hz, vinyl), 7.1—7.4 (m, 9H, aromatic). MS (FD) m/z 307 (M^+).

N,N-Di-4-tolylacrylamide (*4,4'-Me$_2$DPAA*). mp 74—75°C; IR (KBr) 1665, 1618, 1510, 1404, 1330, 1267, 820 cm^{-1}; ^1H NMR (500 MHz) δ 2.34 (s, 6H, CH_3), 5.59 (dd, 1H, J = 2.0, 10.5 Hz, vinyl), 6.20 (dd, 1H, J = 10.5, 17.0 Hz, vinyl), 6.44 (dd, 1H, J = 2.0, 17.0 Hz, vinyl), 7.1—7.2 (m, 8H, aromatic). *Anal.* Calcd for $C_{17}H_{17}NO$: C, 81.24%; H, 6.82%; N, 5.57%. Found: C, 81.24%; H, 6.91%; N, 5.62%.

N,N-Bis(4-butylphenyl)acrylamide (*4,4'-Bu$_2$DPAA*). mp 34—35°C; IR (KBr) 1665, 1618, 1510, 1404, 1330, 1267, 820 cm^{-1}; ^1H NMR (400 MHz) δ 0.92 (t, 6H, J = 7.6 Hz, CH_3), 1.36 (sext, 4H, J = 7.6 Hz, CH_2), 1.59 (quint, 4H, J = 7.6 Hz, CH_2), 2.60 (t, 4H, J = 7.6 Hz, CH_2), 5.59 (dd, 1H, J = 2.0, 10.4 Hz, vinyl), 6.20 (dd, 1H, J = 10.4, 16.8 Hz, vinyl), 6.44 (dd, 1H, J = 2.0, 16.8 Hz, vinyl), 7.1—7.2 (m, 8H, aromatic). *Anal.* Calcd for $C_{23}H_{29}NO$: C, 82.34%; H, 8.71%; N, 4.18%. Found: C, 82.23%; H, 8.94%; N, 4.24%.

Reagents

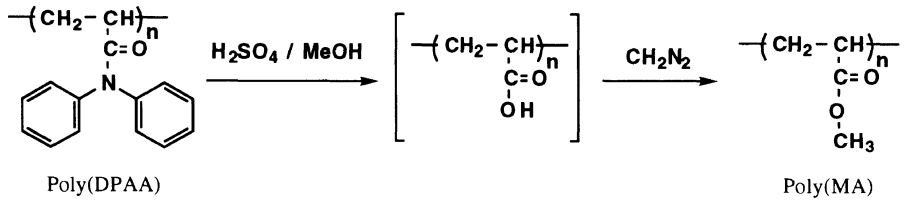
Toluene used for polymerization was purified in the usual manner, mixed with a small amount of *n*-BuLi, and distilled under high vacuum just before use. *n*-BuLi was prepared from 1-chlorobutane and lithium powder in purified heptane. Fluorene (Fl) was recrystallized several times from ethanol and then from hexane. A chiral ligand, (−)-sparteine ((−)-Sp) (Sigma) was dried by stirring overnight with calcium hydride, then distilled under vacuum, and used as a solution in toluene. A radical initiator, diisopropyl peroxydicarbonate (Peroyl) was kindly supplied by NOF Co. and used as a solution in toluene. A chiral initiator (0.2 mol l^{-1}) was prepared by adding *n*-BuLi (1 equiv.) and (−)-Sp (1.2 equiv.) to a toluene solution of fluorene (1 equiv.) at room temperature just before use.[1,4]

Polymerization Procedure

Polymerization was carried out in a glass ampule equipped with a three-way stopcock under dry nitrogen atmosphere. The monomer was first placed in a flame-dried ampule, was then evacuated and flushed with dry nitrogen. A solvent was added to the ampule with a hypodermic syringe, and cooled to a desired temperature. Polymerization was started by the addition of the initiator to the monomer solution, and was terminated by adding a small amount of methanol. The polymers were precipitated in a large amount of methanol, separated by centrifugation, and dried *in vacuo* at 60°C.

Transformation of the Polymer to Poly(MA)

The polymers obtained were transformed to poly(MA) for GPC and ^1H NMR analyses (Scheme 2). To a mixture of the polymer (20 mg) and methanol (0.8 ml) placed in a centrifuge tube (15 ml), was added concentrated sulfuric



Scheme 2.

Table I. Radical and anionic polymerization of substituted DPAAs[a]

Entry	Monomer	Initiator	Yield[b] %	$\overline{DP}$[c]	$\bar{M}_w/\bar{M}_n$[c]	Tacticity[d] (m:r)
1[e]	DPAA	(*iso*-PrOCOO)$_2$	94[f]	52	2.93	15:85
2	4-MeDPAA	(*iso*-PrOCOO)$_2$	81	102	1.69	23:77
3	4,4′-Me$_2$DPAA	(*iso*-PrOCOO)$_2$	59	116	1.67	14:86
4	4,4′-Bu$_2$DPAA	(*iso*-PrOCOO)$_2$	54	108	1.52	12:88
5[e]	DPAA	*n*-BuLi	95	236	2.86	95: 5
6	4-MeDPAA	*n*-BuLi	89	300	7.85	94: 6
7	4-HexDPAA	*n*-BuLi	88	400	11.4	93: 7
8	4,4′-Me$_2$DPAA	*n*-BuLi	91	185	13.3	89:11
9	4,4′-Bu$_2$DPAA	*n*-BuLi	54	74	4.82	77:26

[a] Monomer 0.5 g, toluene 10 ml. Entries 1—4: [M]/[I] = 50, temp = 40°C, time = 24 h. Entries 5—9: [M]/[I] = 20, temp = −98°C, time = 2 h. [b] Methanol insoluble part. [c] Determined by GPC analysis of poly(methyl acrylate) derived from the original polymer (polystyrene standard). [d] Determined by ^{1}H NMR analysis of poly(methyl acrylate) derived from the original polymer. [e] Cited from ref 5. [f] Hexane insoluble part.

acid (1.2 ml) carefully.[5] Then the tube was sealed with a septa rubber cap and was heated under stirring at 90°C for 24 h. After cooling to room temperature, 1 *N* HCl (10—12 ml) was added to precipitate the polymer which was collected by centrifugation and washed with water. Then the polymer was dried *in vacuo* and methylated with an ethereal solution of diazomethane in benzene. The poly(MA) obtained was precipitated in hexane, collected by centrifugation and dried *in vacuo* at 60°C.

RESULTS AND DISCUSSION

Radical and Anionic Polymerization

Table I shows the results of the radical and anionic polymerization of *para*-substituted DPAAs, together with the previous data on DPAA (entries 1 and 5).[5] In the radical polymerization using Peroyl as an initiator at 40°C for 24 h, the obtained polymers were all rich in racemo diad sequence, and poly(4,4′-Bu$_2$DPAA) showed the highest syndiotacticity (r = 88%). These polymers were all soluble in chloroform or THF, and poly(4,4′-Bu$_2$DPAA) even in hexane. The solubility of the obtained polymers was greatly affected by the alkyl substituents introduced to the monomers.

On the other hand, all the polymers obtained by the anionic polymerization using *n*-BuLi as an initiator at −98°C in toluene, were rich in meso diad ($m \geq 77\%$) and the highest isotacticity (m = 95%) was observed for poly(DPAA) (entry 5). These polymers were insoluble in common organic solvents such as chloroform or THF, which may be caused by high isotacticity and degree of polymerization (DP). GPC analysis of poly(MA)s derived from the original polymers showed bimodal molecular weight distribution. The isotacticity of the polymer in the anionic polymerization seems to decrease with an increase of bulkiness of the substituents on the phenyl group, and 4,4′-Bu$_2$DPAA (entry 9) gave the polymer of the lowest isotacticity.

Asymmetric Anionic Polymerization

Table II shows the results of the asymmetric anionic polymerization of *para*-substituted DPAAs in toluene with the complex of (−)-Sp and FlLi as an initiator. The polymerization proceeded in good yields, and the polymers obtained at −98°C showed a higher isotacticity and a larger negative optical rotation than the polymers obtained at −78°C. The polymer with the highest specific rotation ($[\alpha]_{365}^{25} = -423°$) and isotacticity ($m$ = 77%) was obtained for 4,4′-Me$_2$DPAA at −98°C (entry 8). However, the isotacticity and specific rotation of the polymers seem to decrease as the size of alkyl groups increases, and poly(4,4′-Bu$_2$DPAA) showed the lower values.

Clear substituent effect was observed in the solubility of the polymers. The polymers obtained from 4-MeDPAA and 4-HexDPAA, bearing an alkyl group on only one of the phenyl groups, dissolved completely in chloroform. However, the polymers obtained from 4,4′-Me$_2$DPAA and 4,4′-Bu$_2$DPAA, bearing an alkyl group on both of the phenyl groups, were insoluble in chloroform and THF, and the polymers dissolved only when a small amount of trifluoroacetic acid was added to chloroform.[5] Unsymmetrical substitution of the phenyl groups of DPAA enhances the solubility of the polymers.

Table III summarizes the results of the polymerization of DPAAs bearing a methyl group at the *ortho*, *meta*, and *para* position. The results for 3-MeDPAA has been reported in our previous paper.[6] 4-MeDPAA gave the polymer of the highest isotacticity and optical activity, and 2-MeDPAA the lowest ones. As the methyl group of the monomers comes closer to the C=C double bond

Table II. Asymmetric anionic polymerization of 4-substituted DPAAs with (−)-Sp-FlLi[a]

Entry	Monomer	Temp / °C	Yield[b] / %	$\overline{DP}$[c]	$\bar{M}_w/\bar{M}_n$[c]	$[\alpha]_{365}^{25}$[d]	Tacticity[e] (*m*:*r*)
1[f,g]	DPAA	−78	91	48	1.16	−201	64:36
1[f]	DPAA	−98	93	54	1.25	−249	74:26
3	4-MeDPAA	−78	84	51	1.34	−219[h]	64:36
4	4-MeDPAA	−98	90	60	1.20	−395[h]	72:28
5	4-HexDPAA	−78	91	65	1.13	−98[h]	54:46
6	4-HexDPAA	−98	89	65	1.10	−120[h]	62:38
7	4,4′-Me_2DPAA	−78	88	55	1.16	−245	72:28
8	4,4′-Me_2DPAA	−98	79	47	1.11	−423	77:23
9	4,4′-Bu_2DPAA	−78	99	60	1.14	−97	51:49
10	4,4′-Bu_2DPAA	−98	96	62	1.15	−100	53:47

[a] [Monomer]/[(−)-Sp-FlLi] = 20, monomer 0.5 g, toluene 10 ml, time 2 h. [b] Methanol insoluble part. [c] Determined by GPC analysis of poly(methyl acrylate) derived from the original polymer (polystyrene standard). [d] In $CHCl_3$–CF_3CO_2H. [e] Determined by ^1H NMR analysis of poly(methyl acrylate) derived from the original polymer. [f] Cited from ref 5. [g] Polymerization time 1 h. [h] In $CHCl_3$.

Table III. Polymerization of methyl-substituted DPAAs[a]

Entry	Monomer	Initiator	[M]/[I]	Temp / °C	Time / h	Yield[b] / %	$\overline{DP}$[c]	$\bar{M}_w/\bar{M}_n$[c]	$[\alpha]_{365}^{25}$[d]	Tacticity[e] (*m*:*r*)
1	2-MeDPAA	(*iso*-PrOCOO)$_2$	50	40	24	33[g]	55	1.21	—	25:75
2[f]	3-MeDPAA	(*iso*-PrOCOO)$_2$	50	40	24	31	126	1.51	—	36:64
3	4-MeDPAA	(*iso*-PrOCOO)$_2$	50	40	24	81	90	1.52	—	24:76
4	2-MeDPAA	*n*-BuLi	20	−98	2	4	54	1.13	—	83:17
5[f]	3-MeDPAA	*n*-BuLi	20	−98	2	88	302	8.56	—	92: 8
6	4-MeDPAA	*n*-BuLi	20	−98	2	89	300	7.85	—	94: 6
7	2-MeDPAA	(−)-Sp-FlLi	20	−98	2	20	40	1.14	−30	55:45
8[f]	3-MeDPAA	(−)-Sp-FlLi	20	−98	2	75	43	1.10	−142	57:43
9	4-MeDPAA	(−)-Sp-FlLi	20	−98	2	90	60	1.20	−395	72:28

[a] Monomer 0.5 g, toluene 10 ml. [b] Methanol insoluble part. [c] Determined by GPC analysis of poly(methyl acrylate) derived from the original polymer (polystyrene standard). [d] Measured in $CHCl_3$. [e] Determined by ^1H NMR analysis of poly(methyl acrylate) derived from the original polymer. [f] Cited from ref 6. [g] Hexane insoluble part.

Table IV. Asymmetric anionic polymerization of 4-MeDPAA with (−)-Sp-FlLi[a]

Entry	[M]/[I]	Time	Yield[b] / %	$\overline{DP}$[c]	$\bar{M}_w/\bar{M}_n$[c]	$[\alpha]_{365}^{25}$[d]	Tacticity[e] (*m*:*r*)
1[f]	20	5 s	3	46	1.15	−399	87:13
2	20	1 min	40	51	1.08	−657	82:18
3	20	5 min	84	52	1.12	−432	74:28
4	20	2 h	94	60	1.20	−395	72:28

[a] 4-MeDPAA 0.5 g, toluene 10 ml. [b] Methanol insoluble part. [c] Determined by GPC analysis of poly(methyl acrylate) derived from the original polymer (polystyrene standard). [d] In $CHCl_3$. [e] Determined by ^1H NMR analysis of poly(methyl acrylate) derived from the original polymer. [f] 4-MeDPAA 1.0 g, toluene 20 ml.

from 4- to 2-position, the polymerizability seems to decrease.

Since the optically active poly(4-MeDPAA) was soluble in chloroform, the polymerization of 4-MeDPAA with (−)-Sp-FlLi in toluene at −98°C was further investigated (Table IV). Even at a short polymerization time of 5 s, the polymer was collected as a methanol-insoluble fraction. As the polymerization time increased, the polymer yield increased, but the isotacticity of the polymer decreased. The optical activity of the polymers initially increased and then decreased. These results indicate that immediately after starting the polymerization, the initiation and propagation of the polymerization of 4-MeDPAA is very fast, and the polymer produced during this time possesses a high stereoregularity and an optical rotation, while that produced hereafter has a lower stereoregularity and an optical rotation. At least two different propagating species appear to be generated in this polymerization. But since the GPC analysis of the polymers after the transformation into poly(MA) did not show bimodal peak distribution, the different propagating species seem to produce the polymers of similar

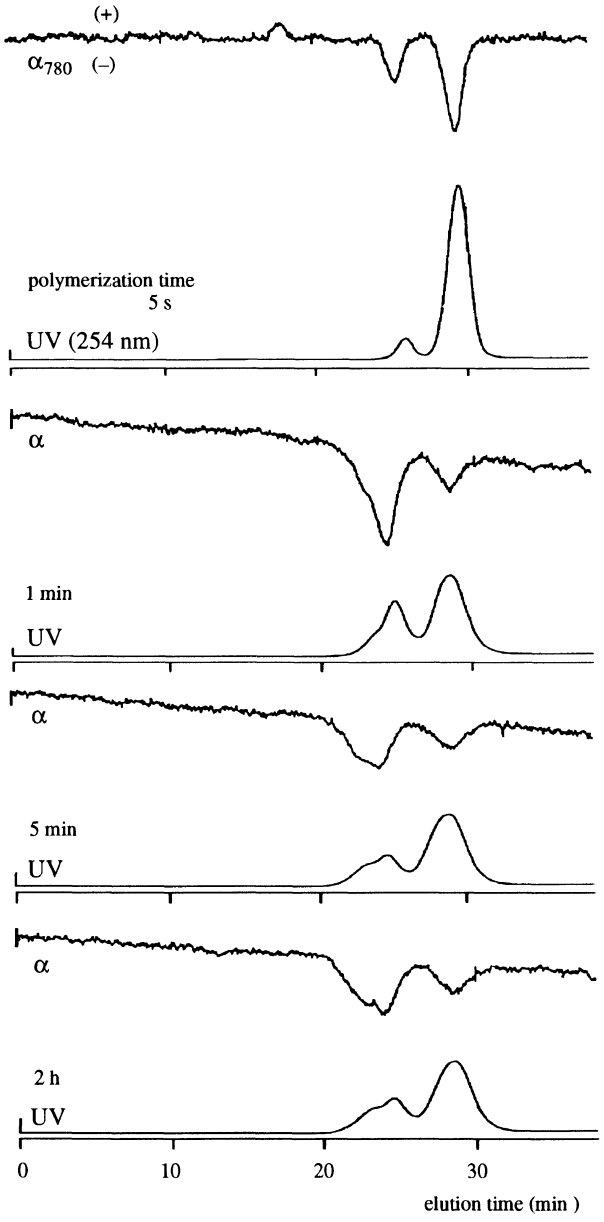


Figure 1. GPC traces of poly(4-MeDPAA)s in Table III, monitored with UV and polarimetric detectors.

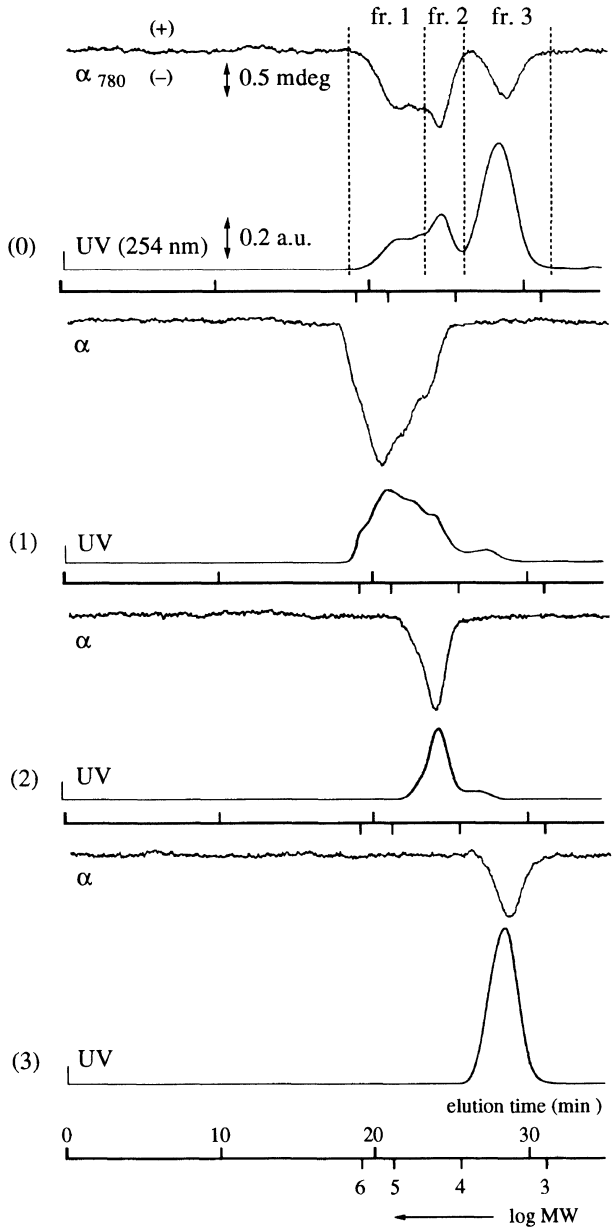


Figure 2. GPC traces of poly(4-MeDPAA) fractionated by GPC; original polymer (0), fraction 1 (1), fraction 2 (2), and fraction 3 (3).

molecular weight and distribution that cannot be distinguished by GPC. The generation of different propagating species may be ascribed to the change in the coordinating state of the bidentate chiral ligand (−)-Sp to a lithium cation. The existence of the polar monomer may change the coordinating state of (−)-Sp. The polymer obtained in the polymerization with *n*-BuLi alone showed a higher isotacticity than the polymer obtained by asymmetric anionic polymerization with (−)-Sp-FlLi. This also indicates that (−)-Sp influences the tacticity of the polymer.

Figure 1 illustrates the GPC traces of the poly(4-MeDPAA)s in Table IV monitored with UV and polarimetric detectors. Multi-modal peaks were observed, and the intensities monitored by the two detectors showed different patterns. The UV absorption found in the higher-molecular-weight region was reduced by the addition of a small amount of trifluoroacetic acid to the sample in chloroform, and the GPC analysis of poly(MA) derived from the original poly(4-MeDPAA) showed a single peak. These results indicate that the multi-modal peak distribution of the poly(4-MeDPAA) in Figure 1 is caused by the association of the polymer chains. From the intensity ratio of the polarimeter to UV detector, we can estimate the optical activity of the polymers. Figure 1 indicates that the fraction of the higher-molecular-weight region (elution time 20—26 min) has a much higher optical activity than that of the fraction of the lower-molecular-weight region (26—31 min). This suggests that the polymer chains of higher optical activity may selectively associate, and this association may induce some conformational change of the polymer chain.

The poly(4-MeDPAA) (entry 3 in Table IV) of a high optical activity was fractionated into three fractions by means of GPC. Figure 2 depicts the GPC traces of the original poly(4-MeDPAA) and the three separated fractions, and the characteristics of the fractionated polymers are summarized in Table V. The specific ro-

Table V. GPC fractionation of poly(4-MeDPAA)[a]

Polymer	$[\alpha]_{365}^{25}$[b]	$\overline{DP}$[c]	$\bar{M}_w/\bar{M}_n$[c]	Tacticity[d] (m:r)
Original[a]	−432	52	1.12	74:26
Fraction 1	−1122	75	1.10	94: 6
Fraction 2	−750	65	1.04	94: 6
Fraction 3	−168	46	1.05	67:33

[a] Entry 3 in Table IV. [b] In $CHCl_3$. [c] Determined by GPC analysis of poly(methyl acrylate) derived from the original polymer (polystyrene standard). [d] Determined by ^1H NMR analysis of poly(methyl acrylate) derived from the original polymer.

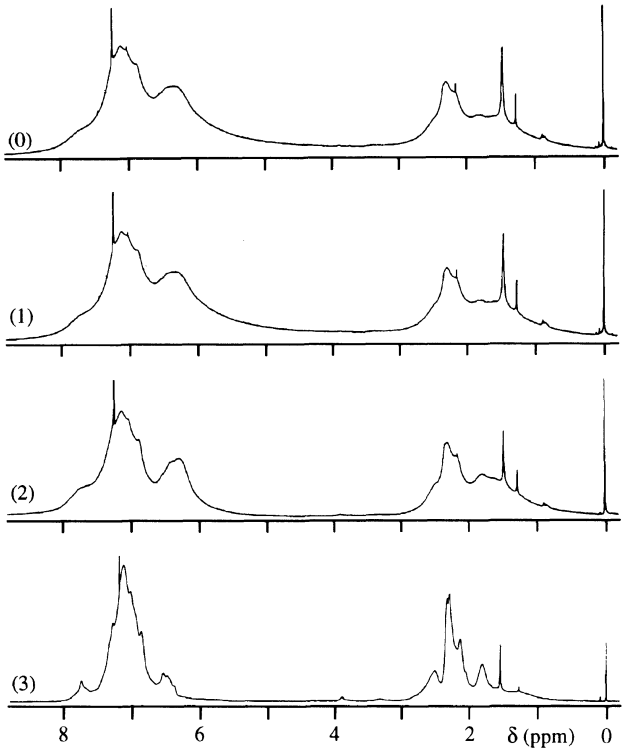


Figure 3. ^1H NMR spectra of poly(4-MeDPAA) fractionated by GPC; original polymer (0), fraction 1 (1), fraction 2 (2), and fraction 3 (3).

tation and *meso* diad content of the fractions decreased as the elution time increased, and fraction 1 showed a high specific rotation ($[\alpha]_{365}^{25} = -1122°$) and an isotacticity ($m = 94\%$). This also indicates that the polymer with high optical activity and tacticity, and the polymer with low optical activity and tacticity must be produced in the polymerization. DP of the fractionated polymers in Table V is close to each other. This suggests that the different propagating species probably produce the polymers of similar molecular weight and distribution which can not be distinguished by GPC as mentioned before. In addition, since the GPC traces of fractions 2 and 3 did not change with time (Figure 2), these fractions do not further associate probably because of low DP for fraction 2 and low isotacticity for fraction 3. Selective association of the polymer chains seems to take place as described before. Additional studies appear to be necessary to clarify this point.

Figure 3 illustrates the ^1H NMR spectra of the above fractionated poly(4-MeDPAA) in $CDCl_3$ at 60°C. Es-

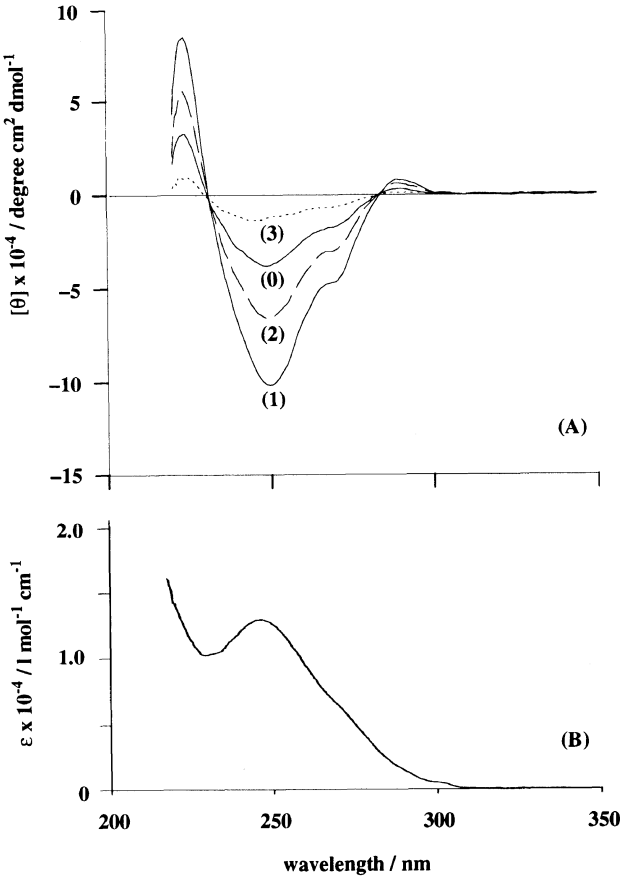


Figure 4. A: CD spectra of poly(4-MeDPAA) fractionated by GPC; original polymer (0), fraction 1 (1), fraction 2 (2), and fraction 3 (3). B: UV spectrum of the original polymer.

timation of the tacticity from the spectra was difficult because of broadening of the peaks.[5] Fractions 1 and 2 show broad peaks, indicating that the mobility of the polymer is restricted probably because of association. Fraction 3 shows a different pattern from those of fractions 1 and 2. This may be due to the difference in the tacticity and association of the polymer chains.

Figure 4(A) depicts the CD spectra of the same fractionated polymers, and Figure 4(B) shows the UV spectrum of the original polymer. Although the CD spectra differ in intensity, the spectral patterns are quite similar, and the intensity clearly increases as the specific rotation increases. A strong CD peak at 250 nm suggests that the phenyl groups exist under a chiral environment. The whole polymer chain appears to be chiral, due to a prevailing one-handed helical conformation produced through the polymerization process. No clear difference in the intensity or in the spectral patterns were found in the UV spectra of the fractionated polymers.

In conclusion, the stereospecificity of the polymerization of the DPAA derivatives decreased as the size of the alkyl groups on the phenyl group increased or as the methyl group gets closer to the C=C double bond of the monomers. Poly(4,4′-Me_2DPAA) showed the highest isotacticity and specific rotation among the polymers obtained in the asymmetric anionic polymerization of the alkyl-substituted DPAAs with (−)-Sp-FlLi as an initiator, but the poly(4,4′-Me_2DPAA) obtained was insoluble in common organic solvents. Fractionation of poly(4-MeDPAA) by GPC showed that the polymer of

a high isotacticity and a high specific rotation was produced together with the polymer of a low stereoregularity and a low specific rotation in the polymerization.

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REFERENCES

1. T. Nakano, Y. Okamoto, and K. Hatada, *J. Am. Chem. Soc.*, **114**, 1318 (1992), and references there in.
2. a) D. V. Badami, *Polymer*, **1**, 273 (1960). b) K. Butler, P. R. Thomas, and G. J. Tyler, *J. Polym. Sci.*, **48**, 357 (1960).
3. Y. Okamoto, M. Adachi, H. Shohi, and H. Yuki, *Polym. J.*, **13**, 175 (1981).
4. Y. Okamoto, H. Hayashida, and K. Hatada, *Polym. J.*, **21**, 543 (1989).
5. K. Shiohara, S. Habaue, and Y. Okamoto, *Polym. J.*, **28**, 682 (1996).
6. S. Habaue, K. Shiohara, T. Uno, and Y. Okamoto, *Enantiomer*, **1**, 55 (1996).
7. A. J. Paine, *J. Am. Chem. Soc.*, **109**, 1496 (1987).