Polymer Journal, Vol. 21, No. 7, pp 543—549 (1989)

# Asymmetric Polymerization of *N,N*-Disubstituted Acrylamides

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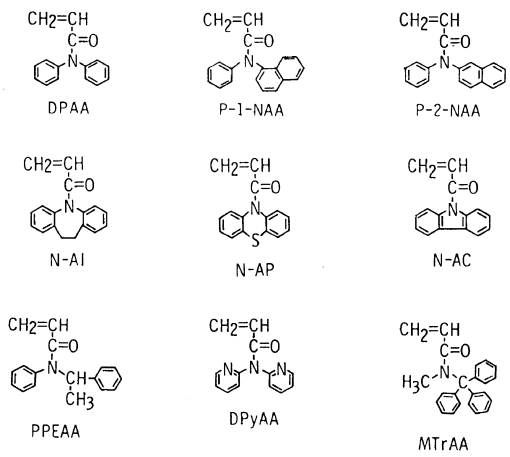
(Received January 31, 1989)

ABSTRACT: The asymmetric polymerization of eleven *N,N*-disubstituted acrylamides was studied with chiral anionic initiators consisting of (−)-sparteine or (2*S*,3*S*)-(+)-1,4-bis(dimethylamino)-2,3-dimethoxybutane and organolithium compounds. Nine of poly(*N,N*-disubstituted acrylamide)s obtained were optically active ($[\alpha]_D^{25}$ $+81.7° \sim -101°$). The chirality of the polymers is ascribed to one-handed helical conformation. Poly(*N,N*-diphenylacrylamide) obtained with (−)-sparteine–fluorenyllithium complex in toluene at −97°C showed the largest negative rotation ($[\alpha]_D^{25}$ $-101°$).

KEY WORDS Asymmetric Polymerization / Optically Active Polymer / Anionic Polymerization / *N,N*-Disubstituted Acrylamide / Helix / (−)-Sparteine / Fluorenyllithium /

Triphenylmethyl methacrylate (TrMA) forms an optically active polymer (PTrMA) arising from the one handed helicity produced in the polymerization with chiral anionic initiators such as the complexes of (−)-sparteine (Sp) or (2*S*,3*S*)-(+)-1,4-bis(dimethylamino)-2,3-dimethoxybutane ((+)-DDB) with organolithium compounds.[1-3] The bulky triphenylmethyl group prevents stereomutation of the helix. It has been also briefly reported that *N,N*-disubstituted acrylamides such as *N,N*-diphenylacrylamide and *N*-phenyl-*N*-(2-naphthyl)acrylamide give optically active polymers, the chirality of which has been ascribed to the one-handed helicity.[4] In the present paper, we report a detailed study on the asymmetric polymerization of eleven *N,N*-disubstituted acrylamides in addition to these acrylamides. The monomers used are *N,N*-diphenylacrylamide (DPAA), *N*-phenyl-*N*-(1-naphthyl)acrylamide (P-1-NAA), *N*-phenyl-*N*-(2-naphthyl)acrylamide (P-2-NAA), *N,N*-di(2-pyridyl)-acrylamide (DPyAA), *N*-phenyl-*N*-(1-phenylethyl)acrylamide (PPEAA), *N*-methyl-*N*-triphenylmethylacrylamide (MTrAA), *N,N*-dicyclohexylacrylamide (DCHAA), *N,N*-dimethylacrylamide (DMAA), *N*-acryloyliminodibenzyl (N-AI), *N*-acryloylphenothiazine (N-AP), and *N*-acryloylcarbazole (N-AC). These monomers except for DCHAA and DMAA gave optically active polymers. It has been reported that *N,N*-disubstituted acrylamides are readily polymerized with anionic initiators to give crystalline polymers.[5]



## EXPERIMENTAL

### *Materials*

DPAA and DCHAA were prepared in the usual manner from acryloyl chloride and double the molar amount of corresponding secondary amine, and purified by recrystallization from diethyl ether and hexane. P-1-NAA, P-2-NAA, N-AI, and PPEAA were obtained by treating a solution of acryloyl chloride in benzene with an equimolar amount of corresponding secondary amine in the presence of *N,N*-dimethylaniline and purified by column chromatography on silica gel or by recrystallization. DPyAA and MTrAA were prepared in the same manner using triethylamine instead of *N,N*-dimethylaniline and purified by recrystallization. N-AC and N-AP were prepared according to the method of Heller and Kingsley.[6] DMAA (Wako Chemical) was distilled under reduced pressure, dried over calcium hydride and distilled under high vacuum just before use.

**Table I.** *N,N*-Disubstituted acrylamides

| Monomer | Yield | Melting point | Elemental analysis (calcd.) | | |
|---|---|---|---|---|---|
| | % | °C | C% | H% | N% |
| DPAA | 64 | 87.0—88.0 | 80.94 | 6.01 | 6.30 |
| | | | (80.36 | 6.25 | 6.25) |
| DCHAA | 16 | 79.5—80.5 | 76.56 | 10.77 | 5.97 |
| | | | (76.60 | 10.64 | 5.96) |
| P-1-NAA | 50 | 101.8—102.2 | 83.41 | 5.68 | 5.10 |
| | | | (83.52 | 5.49 | 5.13) |
| P-2-NAA | 48 | | 83.40 | 5.74 | 4.94 |
| | | | (83.52 | 5.49 | 5.13) |
| N-AI | 30 | 101.3—101.8 | 81.51 | 6.10 | 5.58 |
| | | | (81.93 | 6.02 | 5.62) |
| PPEAA | 70 | 84.6—85.5 | 81.06 | 6.84 | 5.64 |
| | | | (81.27 | 6.77 | 5.58) |
| DPyAA | 23 | 82.5—83.1 | 69.91 | 4.99 | 18.66 |
| | | | (69.03 | 5.31 | 18.58) |
| MTrAA | 24 | 130.0—130.5 | 84.63 | 6.49 | 4.28 |
| | | | (84.40 | 6.42 | 4.28) |
| N-AC | 61 | 50.6—51.5 | 81.75 | 5.13 | 6.38 |
| | | | (81.45 | 4.98 | 6.33) |
| N-AP | 39 | 109.8—110.6 | 71.18 | 4.49 | 5.51 |
| | | | (70.87 | 4.72 | 5.51) |

The melting points and elemental analyses of the monomers are listed in Table I.

Fluorene (Nacalai Tesque) was recrystallized from hexane. Butyllithium (*n*-BuLi) was synthesized from butyl chloride and Li powder in heptane. Fluorenyllithium (FlLi) was synthesized by the reaction of fluorene and an equimolar amount of *n*-BuLi in toluene. (−)-Sparteine (Sigma Chemical Co.) was dried over calcium hydride and distilled under reduced pressure; $[\alpha]_D^{25}$ −18.0° ($c$=4.4 g dl$^{-1}$, ethanol). (+)-DDB (Aldrich Chemical Co.) was purified in the same manner. Chiral initiators were prepared as follows: (−)-Sparteine and FlLi (1.2:1 molar ratio) were mixed in toluene at room temperature just before use, and other initiators were prepared in the same manner. Toluene was purified in the usual manner, mixed with a small amount of *n*-BuLi and distilled under high vacuum just before use.

### *Polymerization*

The polymerization was carried out in a dry glass ampule under dry nitrogen. A solid monomer was placed in the ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this procedure was repeated three times, a solvent was added with a hypodermic syringe. An initiator solution was then added with a syringe to the monomer solution cooled to the temperature of polymerization. The reaction was terminated by the addition of a few drops of methanol. The polymer was precipitated in a large amount of methanol and separated by filtration or centrifugation. When the polymer obtained was partly insoluble in common organic solvents, it was separated with THF or chloroform into soluble and insoluble fractions.

### *Measurements*

Optical rotation was measured with a JASCO DIP-181 polarimeter at 25°C. $^1$H NMR, $^{13}$C NMR, and $^{15}$N NMR spectra were obtained on JNM-MH-100 (100 MHz) and

JEOL-GX500 ($^1$H, 500 MHz; $^{13}$C, 125 MHz; and $^{15}$N, 50 MHz) instruments. Gel permeation chromatographic (GPC) analysis was accomplished on a JASCO TRI ROTAR-II equipped with UV and polarimetric detectors using chloroform as the eluent. Two SHODEX GPC columns, K802.5 (30 cm) and AC80M (50 cm) were connected in series. The molecular weight calibration curves were obtained with polystyrene standards. Circular dichroism (CD) spectra were measured with a JASCO J40-CD apparatus equipped with a computerized data processor.

## RESULTS AND DISCUSSION

Table II shows the results of the polymerization of DPAA under various conditions. DPAA was found to readily give poly(DPAA) in good yields. In general, the polymerization systems in toluene were homogeneous at the early stage of the polymerization but formed a gel as the reaction proceeded. The polymer of high-molecular-weight was insoluble in common organic solvents. Optically active polymers were obtained not only in toluene but also in THF. However, the polymer obtained in THF showed a smaller rotation. The polymer of the highest specific rotation was obtained with (−)-Sp–FlLi in toluene at −97°C. The specific rotation of poly(DPAA) increased with decreasing polymerization temperature.[4]

The polymerization of poly(DPAA) with (−)-Sp–FlLi in toluene at −97°C was further investigated (Table III). Most polymerization was attained within three minutes. Most of the polymer obtained in 12.1% yield was insoluble in chloroform. Higher specific rotation was observed on polymers obtained in a yield less than 56%. The polymer produced in the early stage of the polymerization may have a more stereoregular structure than that in the later stage. This may lead to lower solubility and higher optical activity. The molecular weight of the polymer did not increase with polymer yield and seemed to level off at 3300—3800. A chain transfer or termination reaction appears to take place.

The polymerization of DPAA was carried out at various monomer to initiator ratios using the (−)-Sp–FlLi complex. The results

**Table II.** Polymerization of DPAA in toluene[a]

| Run | Initiator | Temp | Time | Yield | $\bar{M}_n$[b] | $[\alpha]_D^{25}$[c] |
|---|---|---|---|---|---|---|
| | | °C | min | % | | |
| 1 | (−)-Sp–BuLi | −78 | 1 | 89 | | −13.0[d,f] |
| 2 | (−)-Sp–BuLi | −78[e] | 74 | 93 | | −8.1[f] |
| 3 | (−)-Sp–BuLi | −96 | 10 | 89 | 3880 | −50.9[f] |
| 4 | (−)-Sp–FlLi | −78 | 120 | 80 | 3200 | −34.1 |
| 5 | (−)-Sp–FlLi | −97 | 120 | 82 | 3250 | −61.7 |
| 6 | (−)-Sp–DPA–Li[g] | −97 | 120 | 61 | 4050 | −18.1 |
| 7 | (+)-DDB–DPEDA–Li[h] | −78 | 300 | 83 | 13790 | −3.2 |
| 8 | (+)-DDB–DPEDA–Li[h] | −97 | 300 | 86 | 8010 | −1.5 |

[a] Solvent/monomer = 20 ml g$^{-1}$, [M]/[I] = 20. The results in runs 1—3 are reported in ref 4.
[b] Determined by GPC.
[c] In $CHCl_3$.
[d] A part of the polymer insoluble in THF and $CHCl_3$; THF-soluble part (94%).
[e] Solvent, THF.
[f] In THF.
[g] $Ph_2N$–Li.
[h] $PhNHCH_2CH_2N(Ph)$–Li.

**Table III.** Polymerization of DPAA with (−)-Sp–FlLi in toluene at −97°C[a]

| Time | Yield | $\bar{M}_n$[b] | $[\alpha]_D^{25}$[c] |
|---|---|---|---|
| s | % | | |
| 2 | 12.1 | 2080[d] | |
| 4 | 37.1 | 2630 | −98.7 |
| 7 | 42.2 | 2710 | −101 |
| 30 | 56.0 | 3760 | −97.4 |
| 60 | 67.4 | 3380 | −71.6 |
| 120 | 73.0 | 3520 | −63.3 |
| 3600 | 82.4 | 3250 | −61.7 |

[a] Solvent/monomer = 20 ml g$^{-1}$, [M]/[I] = 20.
[b] Determined by GPC.
[c] In $CHCl_3$.
[d] $CHCl_3$-soluble part.

**Table IV.** Polymerization of DPAA with (−)-Sp–FlLi in toluene at −97°C[a]

| Run | [M]/[I] | Time h | Yield[b] % | $\bar{M}_n$[c] | $[\alpha]^{25}$[d] 589 nm | 435 nm |
|---|---|---|---|---|---|---|
| 9 | 1 | 1 | 27.9 | 2550 | −57.6 | −161 |
| 10 | 2 | 1 | 25.7 | 2520 | −82.7 | −240 |
| 11 | 10 | 1 | 40.9 | 2490 | −79.2 | −231 |
| 12 | 15 | 1 | 68.5 | 2870 | −87.1 | −261 |
| 13 | 20 | 1 | 82.4 | 3250 | −61.7 | −181 |
| 14 | 30 | 1 | 93.4 | 3450 | −41.0 | −123 |

[a] Solvent/monomer = 20 ml g$^{-1}$.
[b] MeOH-insoluble part.
[c] Determined by GPC.
[d] In $CHCl_3$.

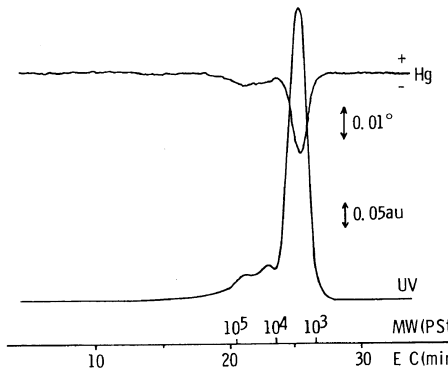



**Figure 1.** GPC curve of poly(DPAA) ($[\alpha]_D^{25}$ −61.7°; No. 5 in Table II) obtained by (−)-Sp–FlLi in toluene at −97°C.

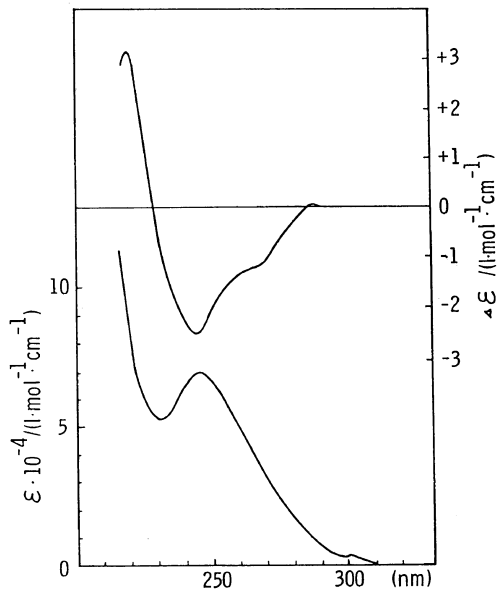



**Figure 2.** UV and CD spectra of poly(DPAA) ($[\alpha]_D^{25}$ −61.7°; No. 5 in Table II) in chloroform.

are shown in Table IV. The fact that methanol-insoluble polymer was obtained even when the monomer to initiator ratios were one or two indicates that in this polymerization, the propagation rate is much faster than the initiation. The yield and the molecular weight of the polymer insoluble in methanol increased with the molar ratio of DPAA to FlLi. The specific rotation of poly(DPAA) was larger when the molar ratio was between 2—15.

Figure 1 illustrates the GPC curve of poly(DPAA) (No. 5 in Table II) monitored with UV and polarimetric detectors. The UV detector monitored at 254 nm showed a trimodal GPC curve, and a polarimetric detector showed a negative peak whose pattern is different from that of the UV curve. Comparison of the intensities of these two curves indicates that specific rotation of the polymer of high-molecular-weight is greater than that of low-molecular-weight polymer. This suggests that the optical activity of this polymer may not be due to the configurational chirality of end groups but rather conformational chirality.

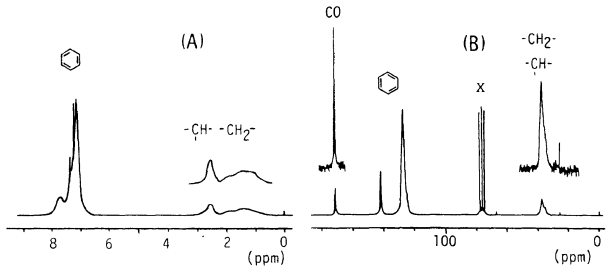



**Figure 3.** NMR spectra of poly(DPAA) obtained by AIBN in toluene at 60°C for 24 h; (A) $^1$H, 500 MHz, $CDCl_3$, 55°C; (B) $^{13}$C, 125 MHz, $CDCl_3$, 55°C. "X" peak due to the solvent.

The GPC curve of the poly(DPAA) with larger negative rotation ($[\alpha]_D^{25}$ −87°; No. 12 in Table IV) was similar to Figure 1. The intensity of polarimetric peak of the main peak was 1.23 times as strong as that of Figure 1. The complicated GPC curve suggests that there exist a few different propagating species in the polymerization.

The UV and CD spectra of poly(DPAA) (No. 5 in Table II) are depicted in Figure 2. The broad peak at about 270 nm indicates that the phenyl group in the polymer is under certain chiral circumstance. The split peaks at 230 nm suggest that amide groups may also exist under chiral circumstance.

The $^1$H and $^{13}$C NMR spectra of poly(DPAA) are illustrated in Figure 3. The broad $^1$H NMR peaks indicate that the polymer chain is rigid. The $^{13}$C NMR spectrum showed no clear splitting pattern due to the tacticity of the polymer. Therefore, the tacticity of poly(DPAA) is not clear. To obtain more information on the tacticity, the stereoregularity of two poly(DMAA) samples which were prepared by radical and anionic polymerizations were investigated. The tacticity of this polymer has been investigated by Gia and McGrath.[7] They assigned the tacticity on the basis of the $^1$H NMR signals of N-methyl groups. We tried to assign the tacticity by 125 MHz $^{13}$C and 50 MHz $^{15}$N NMR spectra. However, no clear splitting due to tacticity was obtained.

The optical activity of poly(DPAA) (No. 5 in Table II) slowly decreased in chloroform at 25°C. However, after about a 10% decrease, the solution became turbid and measurement of optical activity was impossible. In the previous paper,[4] we reported the change of optical activity of poly(DPAA) (No. 3 in Table II) in solution. The toluene-insoluble but THF-soluble polymer with $[\alpha]_D^{25}$ −61.6° was completely dissolved in sulfuric acid in 15 min and showed $[\alpha]_D^{25}$ −6° immediately after dissolution. The rotation decreased to 0° after about 2 h and reached +7° after about 8 h. The $^1$H NMR peak of poly(DPAA) in $D_2SO_4$ became sharper with time and did not change after 199 h. The intrinsic viscosity in $H_2SO_4$ decreased from $\eta_{sp}/c=0.259$ dl g$^{-1}$ to a constant value ($\eta_{sp}/c=0.112$ dl g$^{-1}$) after 141 h. These results may be due to conformational change in poly(DPAA).

Although the tacticity of poly(DPAA) is not clear at present time, the origin of the chirality of this polymer may be associated with helicity as reported previously in the case of optically active PTrMA. The polymer chain may prevail as either left- or right-handed helix. The rotation of this polymer may correspond to the rotation of the excess helical polymer chain yielded during polymerization due to the chirality of the ligand. The specific rotation of poly(DPAA) obtained in toluene was much smaller than that of PTrMA obtained under the same reaction conditions. One-handedness of poly(DPAA) might be low compared with that of PTrMA. In the case of methacrylates, a

**Table V.** Polymerization of *N,N*-disubstituted acrylamides with (−)-Sp-FlLi in toluene[a]

| Run | Monomer | Temp | [M] | Time | Yield | $\bar{M}_n$[b] | $[\alpha]^{25}$[c] | |
|---|---|---|---|---|---|---|---|---|
| | | °C | [I] | h | % | | 589 nm | 435 nm |
| 15 | N-AI | −97 | 20 | 2 | 54.4 | 2520[d] | −0.5[d] | −2.5[d] |
| 16 | N-AP | −78 | 20 | 4 | 84.3 | 2890[d] | −1.5[d] | −4.7[d] |
| 17 | N-AP | −97 | 20 | 5 | 61.1 | 1780 | +8.2 | +24.3 |
| 18 | N-AC | −97 | 10 | 2 | 85.1 | 1200[d] | +57.4[d] | +147[d] |

[a] Solvent/monomer = 20 ml g$^{-1}$.
[b] Determined by GPC.
[c] In $CHCl_3$.
[d] $CHCl_3$-soluble part.

**Table VI.** Polymerization of *N,N*-disubstituted acrylamides with (−)-Sp-BuLi in toluene[a]

| Run | Monomer | Temp | Time | Yield | $[\alpha]^{25}$[b] | |
|---|---|---|---|---|---|---|
| | | °C | min | % | 589 nm | 435 nm |
| 19 | P-1-NAA | 0 | 30 | 84 | +7.5 | +20.8 |
| 20 | P-1-NAA | −78 | 60 | 64 | +8.7 | +21.2 |
| 21 | P-2-NAA | −78 | 1 | 91 | +81.7 | +208 |
| 22 | P-2-NAA | −96 | 60 | 70 | +76.2 | +185 |
| 23 | DPyAA[c] | −97 | 300 | 65 | −23.7[d] | −64.8[d] |
| 24 | PPEAA[c] | −97 | 120 | 55 | −0.3[e] | −0.9[e] |
| 25 | MTrAA | −78 | 30 | 45 | −2.4 | −5.3 |
| 26 | MTrAA[f] | −78 | 180 | 100 | −6.4 | −13.5 |

[a] Solvent/monomer = 20 ml g$^{-1}$, [M]/[I] = 20.
[b] In THF.
[c] Initiator, (−)-Sp-FlLi.
[d] In $CHCl_3$–$CHCl_2COOH$ (22 : 1).
[e] $CHCl_3$-soluble part.
[f] Initiator, (+)-DDB-$(CH_3)_2CHNH$-  -N(Ph)Li.

large ester group like triphenylmethyl is necessary to form a stable helical polymer, and diphenylmethyl methacrylate can not form a stable helical polymer.[8] In the case of DPAA, the *N,N*-diphenylamino group is closer with respect to the C=C double bond than the diphenylmethyl group of the methacrylate. This closer position of *N,N*-diphenylamino group may make the polymer conformationally more rigid.

Table V shows the results of the polymerization of N-AI, N-AP, and N-AC. N-AP and N-AC formed optically active polymers and N-AI gave a polymer with low optical activity. These monomers have bridge structures between two phenyl groups. The optical rotation of these polymers increased with decrease in the bridge bond. N-AC gave a large positive polymer with a low-molecular-weight.

Table VI shows the results of the polymerization of P-1-NAA, P-2-NAA, DPyAA, PPEAA, and MTrAA. These monomers have aromatic groups such as naphthyl, pyridyl, and triphenylmethyl group. P-1-NAA and P-2-NAA gave dextrorotatory polymers. DPyAA and MTrAA gave polymers of negative rotation. PPEAA has an asymmetric carbon on the N-substituted group. The optical rotation

of this polymer was low. We also asymmetric-selectively (enantioasymmetrically) polymerized this monomer using anionic initiators such as (−)-Sp–FlLi and (−)-Sp–cyclohexylmagnesium bromide.[9] However, the enantiomer excess (*e.e.*) of unreacted monomer was very low. Almost no enantiomer selection was attained.

DCHAA and DMAA which do not have an aromatic group, gave optically inactive polymers ($[\alpha]_D^{25}$ 0°).[4] This may be due to the fact that the steric hindrance of the side groups in these polymers is not large enough to maintain the chiral conformation in the polymerization, or that a helical structure was not preferentially formed during the polymerization.

Several *N*,*N*-disubstituted acrylamides gave optically active polymers, probably arising from one-handed helicity. The optical rotation of these polymers varied with the *N*,*N*-disubstituted group. However, the tacticity and one-handedness of these polymers are not clear. Further study is necessary to clarify this.

*Acknowledgment.* The authors wish to thank Mr. Hajime Shohi and Mr. Takahiro Takeda for their experimental supports.

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