

SHORT COMMUNICATION

Asymmetric Polymerization of *N,N*-Disubstituted Acrylamides

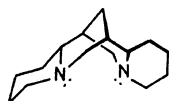
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We have recently reported that triphenylmethyl methacrylate (TrMA) forms an optically active polymer (PTrMA) in the polymerization initiated with chiral anionic catalysts such as (-)-sparteine-butyllithium (BuLi) complex and lithium (*R*)-*N*-(1-phenylethyl)anilide.^{1,2} This is the first example of an



(-)-sparteine

optically active vinyl polymer whose chirality is caused only by helicity. This isotactic helical structure, produced in the polymerization, could be maintained stably in solution mainly as a result of the sterical influence from the bulky triphenylmethyl groups. TrMA is an α,α -disubstituted monomer and optically active PTrMA is useful for the optical resolution of various *racemic* compounds.³ This prompted us to check whether or not an optically active polymer could be obtained from a monosubstituted prochiral vinyl monomer.

This paper describes the anionic polymerization of five *N,N*-disubstituted acrylamides, *N,N*-diphenyl- (DPAA), *N*-phenyl-*N*-1-naphthyl- (1-NAA), *N*-phenyl-*N*-2-naphthyl- (2-NAA), *N,N*-dicyclohexyl- (DCHAA), and *N,N*-dimethylacrylamide (DMAA), by (-)-sparteine-BuLi catalyst. The first three monomers gave optically active polymers. It has been reported that *N,N*-disubstituted acrylamides are readily polymerized with anionic catalysts to give crystalline polymers.⁴

DPAA and DCHAA were prepared in the usual manner from acryloyl chloride and two moles of corresponding secondary amine and purified by recrystallization. 1-NAA and 2-NAA were obtained by treating a solution of acryloyl chloride in benzene with one mole of appropriate *N*-phenyl-*N*-naphthylamine in the presence of *N,N*-dimethylaniline and purified by liquid chromatography on silica gel. The preparation of catalyst and the procedure of polymerization have been described previously.^{1,2} Optical rotation was measured with a JASCO DIP-181 polarimeter in a 10-cm cell. Specific rotation is expressed in terms of the conventional unit, degree cm^2 (10 g)⁻¹.

Table I shows the results of the polymerization of DPAA by (-)-sparteine-BuLi catalyst in toluene and tetrahydrofuran (THF). DPAA readily polymerized to give its polymer almost quantitatively. A considerable part of the polymer was insoluble in THF when the molar ratio of DPAA to BuLi was greater than 100. This may be due to the formation of a high-molecular-weight polymer. THF-insoluble polymers were soluble in sulfuric acid, but insoluble in other common organic solvents. Optically active polymers were obtained not only in toluene but in THF. Polymers of high specific rotation were formed in toluene at -96°C . The rotation of the THF-soluble polymer did not change in THF at 25°C at least for 4 h. However, the rotation increased slightly with time at 50°C and reached a constant value after about 3 h. The rotation of the THF-insoluble polymers in sulfuric acid did not change for 24 h at 25°C . It took about 1 h to dissolve

Table I. Polymerization of *N,N*-diphenylacrylamide by (–)-sparteine–BuLi catalyst in toluene^a

Run no.	Temp °C	[DPAA]	Time min	Yield %	THF-soluble polymer		THF-insoluble polymer	
		[BuLi]			Yield/%	$[\alpha]_D^{25b}$	Yield/%	$[\alpha]_D^{25c}$
1	0	20	10	93	81	–0.8	12	—
2	0	200	28	99	22	0	77	–1.4
3	–78	20	1	89	84	–13.0	5	—
4	–78 ^d	20	74	93	93	–8.1	0	—
5	–78	50	10	99	85	–4.2	14	–6.2
6	–78	100	14	99	50 ^e	+2.6	49 ^f	–7.4
7	–96	20	10	89	89	–50.9	0	—
8	–96	20	60	93	93 ^g	–44.2	0	—

^a Monomer, 1.5 g; solvent, 15 ml.^b In THF, $c = \sim 1 \text{ g dl}^{-1}$.^c In sulfuric acid, $c = \sim 1 \text{ g dl}^{-1}$.^d Solvent, THF.^e $[\eta] = 0.17 \text{ dl g}^{-1}$ (sulfuric acid, 30°C, after 24 h).^f $[\eta] = 0.27 \text{ dl g}^{-1}$ (sulfuric acid, 30°C, after 24 h).^g This was fractionated with toluene; soluble part (34%) $[\alpha]_D^{25} - 11.4^\circ$ (THF), insoluble part (66%) $[\alpha]_D^{25} - 61.6^\circ$ (THF).**Table II.** Polymerization of 1-NAA, 2-NAA, DCHAA, and DMAA (–)-sparteine–BuLi catalyst in toluene^a

Run no.	Monomer	Temp	Time min	Yield %	$[\alpha]^{25}$ (toluene)	
		°C			At 589 nm	At 435 nm
11	1-NAA	0	30	84	+7.5	+20.8
12	1-NAA	–78	60	64	+8.7	+21.2
13	1-NAA	–96	60	67 ^b	—	—
14	2-NAA	0	60	94 ^c	—	—
15	2-NAA	–78	1	91	+81.7	+208
16	2-NAA	–78 ^d	60	87	+51.1	+117
17	2-NAA	–96	60	70	+76.2 ^e	+185
18	DCHAA	–78	10	98	0 ^f	0 ^f
19	DMAA	–78	10	93	0 ^g	0 ^g

^a Solvent/monomer = 20 ml/g; [monomer]/[BuLi] = 20.^b A part of the polymer was insoluble in toluene and THF; THF-soluble part (69%) $[\alpha]_D^{25} + 1.8^\circ$ (THF), THF-insoluble part (31%) $[\alpha]_D^{25} + 5.8^\circ$ (H₂SO₄, after 20 h).^c A part of the polymer was insoluble in toluene and THF; THF-soluble part (66%) $[\alpha]_D^{25} - 32.1^\circ$ (THF), THF-insoluble part (34%) $[\alpha]_D^{25} + 1.0^\circ$ (H₂SO₄, after 20 h).^d Solvent, THF.^e $[\alpha]_D^{25} + 15.4^\circ$ (H₂SO₄, after 20 h).^f In H₂SO₄.^g In CH₃OH.

the polymer (0.10 g) completely in sulfuric acid (10 ml). In the case of the THF-soluble polymer, the rotation in sulfuric acid depended very much on

time after dissolution. For instance, the toluene-insoluble but THF-soluble polymer (No. 8) with $[\alpha]_D^{25} - 61.6^\circ$ was completely dissolved in sulfuric

acid in 15 min and showed $[\alpha]_D^{25} -6^\circ$ immediately after dissolving. The rotation decreased to 0° after about 2 h and reached $+7^\circ$ after about 8 h. Although the cause for these rotational changes in sulfuric acid is not clear at the present time, the origin of chirality of the polymers may result from helicity, as was observed for optically active poly(triphenylmethyl methacrylate). The helical structure prevalent in one screw sense probably comes about during polymerization due to the chirality of (-)-sparteine.^{1,2} The specific rotation of poly(DPAA) obtained in toluene was much smaller than that of poly(triphenylmethyl methacrylate) obtained under the same reaction conditions and opposite in sign. In Run No. 6, THF-soluble polymer showed a positive rotation, indicating that the polymers produced by the (-)-sparteine-BuLi catalyst may perhaps be a mixture of polymers having positive and negative rotations. There seems to exist two different types of active centers which are not enantiomeric to each other. One forms a positive polymer and its reactivity is low, and the other forms a negative polymer and its reactivity is high. When the concentration of BuLi is high, a mixture of these polymers will be obtained as a THF-soluble part, but when it is low, the negative polymer will become insoluble in THF because of its high molecular weight.

Table II shows the results of the polymerization of 1-NAA, 2-NAA, DCHAA, and DMAA. 1-NAA and 2-NAA gave optically active polymers and most polymers showed positive rotation which is opposite to that of the poly(DPAA). A part of the poly(2-NAA) obtained at 0°C was insoluble in THF and the other part, soluble in THF, showed a negative rotation. A phenomenon similar to Run No. 6 seems to occur by changing the temperature of the polymerization, although the details for this are not clear at present time. The rotation of poly(1-NAA) and poly(2-NAA) in THF did not change at least for several hours at room temperature. However, at 50°C the rotation of poly(2-NAA) increased slowly by about 10% and reached a constant value after 8 h.

The circular dichroism (CD) spectra of these optically active polymers showed peaks at wave lengths where the absorptions appeared in their electronic spectra. This indicates that the phenyl and naphthyl groups in the polymers also receive under chiral influence. Positive and negative poly(2-NAA) showed CD spectra that were mirror images of each other. This indicates that both the polymers are enantiomeric.

Poly(DCHAA) and poly(DMAA) were found to be optically inactive. This may be due to the fact that either the sterical hindrance of the side groups in these polymers is not large enough to maintain the chiral conformation formed in the polymerization, or that one of chiral structures was not formed preferentially in the polymerization.

In the case of α,α -disubstituted TrMA, the α -methyl group in addition to a bulky triphenylmethyl group may also play an important role in maintaining the helical conformation of the polymer. The monomers in the present work are monosubstituted. The *N,N*-diphenylamino group in DPAA is smaller than triphenylmethyl group, but the former is in the β -position with respect to the C=C double bond while the latter is in the γ -position. This close position of the branched *N,N*-diphenylamino group is likely to make it possible for DPAA to form an optically active polymer. There seems to be the possibility for obtaining several other optically active vinyl polymers of this type.

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