

Stereospecific Polymerization of *N,N*-Diphenylacrylamide

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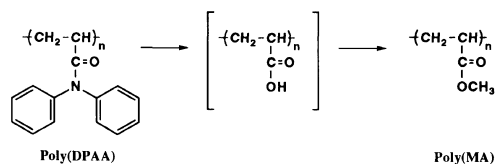
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ABSTRACT: *N,N*-Diphenylacrylamide (DPAA) was polymerized with anionic and radical initiators in toluene and tetrahydrofuran. The tacticity of the obtained polymers (poly(DPAA)) was unable to be determined directly by NMR spectroscopy. Therefore, poly(DPAA) was carefully converted to poly(acrylic acid) by solvolysis in a mixture of concentrated sulfuric acid and methanol (60:40; by volume) at 90°C for 24 hours, followed by methylation with diazomethane. Under suitable conditions, the transformation was performed without change (racemization) of tacticity of the polymers. Diad tacticity of the derived poly(methyl acrylate) was determined by ¹H NMR spectroscopy. Anionic polymerization using butyllithium in toluene afforded a polymer rich in *meso* diad (*m*=0.95), and that in tetrahydrofuran *racemo* diad (*r*=0.66). Radical polymerization in toluene afforded a polymer with the highest *racemo* diad content (*r*=0.85).

KEY WORDS Stereospecific Polymerization / Anionic Polymerization / *N,N*-Diphenylacrylamide / Tacticity / Racemization / Poly(methyl acrylate) /

N,N-Disubstituted acrylamides are known to yield crystalline polymers by anionic polymerization, and the tacticity of the obtained polymers is considered isotactic.¹ It has also been reported that *N,N*-disubstituted acrylamides bearing bulky substituents such as *N,N*-diphenylacrylamide (DPAA) afford optically active polymers in the anionic polymerization with chiral initiators.^{2,3} However, no information on tacticity of poly(DPAA)s is available by NMR spectroscopy. Precise determination of the tacticity of poly(*N,N*-disubstituted acrylamides), even poly(*N,N*-dimethylacrylamide),⁴ appears much more difficult than that of polyacrylates or polymethacrylates. The diad tacticity of poly(methyl acrylate) (poly(MA)) can be readily determined by ¹H NMR spectroscopy.⁵ Therefore, we converted poly(DPAA) to poly(MA) via poly(acrylic acid) and found suitable conditions (Scheme 1). By this method, we determined the diad tacticity of the poly(DPAA)s obtained under various conditions.



Scheme 1.

EXPERIMENTAL

Measurements

¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded on a Varian VXR500S spectrometer. Diad tacticity of poly(MA)s was evaluated from the signals of β -methylene protons, measured in chloroform-*d* at 60°C using tetramethylsilane as an internal standard.⁵ The molecular weights of the polymers were measured by gel permeation chromatographic (GPC) analysis on a JASCO BIP-I chromatograph equipped with a DG-980-

50 degasser and a 830-RI refractive index detector. Two commercial columns (TSK G4000H₈ 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.

Materials

Toluene was purified in the usual manner, mixed with a small amount of *n*-BuLi, and distilled under high vacuum just before use. Tetrahydrofuran (THF) was distilled over sodium metal using benzophenone ketyl as indicator, and distilled over lithium aluminum hydride under high vacuum just before use. Butyllithium (*n*-BuLi) was prepared from 1-chlorobutane and lithium powder in heptane. A radical initiator perloyl was kindly supplied by N.O.C. and used as a toluene solution. *N,N*-Diphenylacrylamide was prepared by reaction of acryloyl chloride with diphenylamine in the presence of *N,N*-dimethylaniline and was purified by recrystallization from diethyl ether and then from hexane; mp 87.5—88.0°C (lit. mp 87.0—88.0°C).³

Polymerization Procedure

Polymerization was carried out in a glass ampule equipped with a three-way stopcock under a dry nitrogen atmosphere. The procedure was the same as before.^{2,3} The monomer was first placed in a dry ampule, which was then evacuated and flushed with dry nitrogen. The solvent was added with a syringe, and cooled to the desired temperature. The polymerization was started by the addition of the initiator to the monomer solution. Polymerization was terminated by adding a small amount of methanol and then the polymer was precipitated in a large amount of methanol. The polymer was separated by centrifugation and dried *in vacuo* at 60°C for 3 hours.

Asymmetric anionic polymerization was performed in the same procedure as written in the literature,³ using the complex of (–)-sparteine and fluorenyllithium as an initiator.

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Transformation of Poly(DPAA) to Poly(MA)

The obtained polymer was converted to poly(MA) for ^1H NMR and GPC analyses. Sulfuric acid (1.2 ml) was carefully added to a mixture of poly(DPAA) (20 mg) and methanol (0.8 ml) in a 15 ml centrifuge tube with a magnetic stirring bar. The tube was capped with a septa rubber cap and heated with stirring at 90°C for 24 hours. After cooling, aqueous hydrochloric acid (1*N*, 10–12 ml) was added to the mixture. The precipitated polymer was washed with hydrochloric acid, collected by centrifugation (total 3 times), dried *in vacuo* at 40°C for 3 hours, and methylated in benzene with an ethereal solution of diazomethane. The poly(MA) was precipitated by the addition of an excess of hexane, separated by centrifugation, and dried *in vacuo* at 60°C for 6 hours.

Transformation of optically active poly(DPAA)s was done with a small modification to dissolve the polymer, by adding 0.05 ml of chloroform to the reaction mixture at the beginning and after 6 hours of reaction. After 24 hours, the polymers were treated in the same way as described before and the tacticity of the polymers was estimated by ^1H NMR analysis.

RESULTS AND DISCUSSION

Stereoregularity of Poly(DPAA)

Figure 1 demonstrates the ^1H and ^{13}C NMR spectra of the poly(DPAA) prepared by radical polymerization using perloyl (entry 9 in Table II). Broad peaks in the ^1H NMR spectrum indicate that the polymer chain is rigid, and the ^{13}C NMR spectrum shows no clear splitting pattern due to the tacticity of the polymer in contrast to other poly(*N,N*-disubstituted acrylamide)s.⁴ The diad stereoregularity of poly(methyl acrylate) (poly(MA)) can be determined by NMR analysis.⁵ Therefore, we tried to transform poly(DPAA) into poly(MA) without changing the tacticity which could occur by the isomerization at the stereogenic center.

Table I lists the results of the transformation of poly(DPAA) (entry 3 in Table II) to poly(MA) under various conditions. Hydrochloric acid is effective for the solvolysis of poly(triphenylmethyl methacrylate)⁶ and some poly(acrylamide)s.⁷ However, no reaction took place in the case of poly(DPAA) (entry 1 and 2), probably due to insolubility of poly(DPAA). Poly(DPAA) is completely dissolved in sulfuric acid.³ The solvolysis reaction smoothly proceeded in sulfuric acid containing water or methanol (entry 4–7). However, the tacticity of the poly(MA) obtained by the solvolysis in sulfuric acid–water followed by the methylation with diazomethane was almost atactic, suggesting that isomerization of stereogenic center took place. However, the reaction with sulfuric acid–methanol (60:40, v/v) resulted in a highly isotactic poly(MA) ($m = 95\%$).

To confirm whether any change occurs in the stereochemistry of the main chain of poly(DPAA) during the transformation in sulfuric acid, transformation with sulfuric acid- d_2 was conducted by aid of ^1H NMR spectroscopy. First, change in the tacticity on poly(MA) with isotactic diads ($m = 91\%$) was investigated (Figure 2).⁸ The ^1H NMR spectrum of the main chain region of poly(MA) after heating at 90°C for 1 hour in $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ (90:10), measured at 90°C is illustrated in Figure

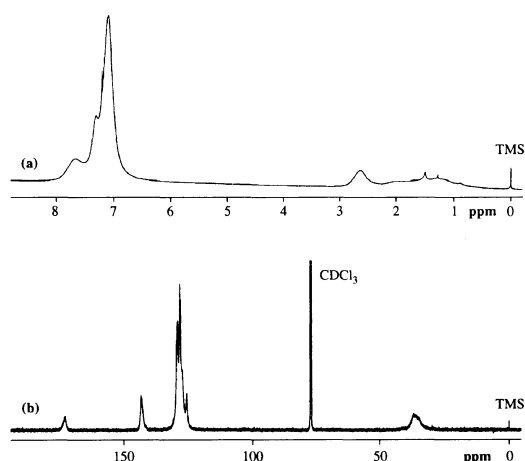


Figure 1. 500 MHz ^1H NMR (a) and 125 MHz ^{13}C NMR (b) spectra of the radically obtained poly(DPAA) (entry 9 in Table II) measured in chloroform- d , at 60°C and 27°C , respectively.

Table I. Tacticity of poly(MA) derived from poly(DPAA)^a

Entry	Solvolysis condition	Diad tacticity (<i>m</i> : <i>r</i>)
1	12 <i>N</i> HCl–MeOH (reflux) ⁶	No reaction
2	12 <i>N</i> HCl–Dioxane (110°C) ⁷	No reaction
3	H_2SO_4	Decomposed ^b
4	H_2SO_4 –MeOH (90:10)	46:54
5	H_2SO_4 –MeOH (70:30)	75:25
6	H_2SO_4 –MeOH (60:40)	95:5
7	H_2SO_4 –MeOH (50:50)	No reaction
8	H_2SO_4 – H_2O (90:10)	48:52
9	H_2SO_4 – H_2O (80:20)	^c
10	H_2SO_4 – H_2O (70:30)	No reaction

^a Poly(DPAA) obtained in toluene using *n*-BuLi at -98°C , 2 h (entry 3 in Table II). Reaction time 24 h. ^b Poly(MA) not recovered. ^c Not completely transformed to poly(MA).

Table II. Anionic polymerization of DPAA using *n*-BuLi^a

Entry	Solvent	Temp/ $^\circ\text{C}$	Yield/% ^b	DP ^c	\bar{M}_w/\bar{M}_n ^c	Tacticity ^d (<i>m</i> : <i>r</i>)
1	Toluene	0	94	85	7.04	94:6
2	Toluene	-40	92	144	8.50	95:5
3	Toluene	-98	95	236	2.86	95:5
4	THF	0	84	62	1.16	47:53
5	THF	-40	88	85	1.27	46:54
6	THF	-78	87	142	1.62	43:57
7	THF	-98	87	207	1.88	38:62
8	THF	-110	43	218	1.86	34:66
9 ^e	Toluene	40	94	52	2.93	15:85

^a $[\text{M}]/[\text{I}] = 20$, time 2 hours. ^b Methanol insoluble part. ^c Determined by GPC using poly(methyl acrylate) derived from the original polymer and polystyrene standards. ^d Determined by ^1H NMR using poly(methyl acrylate) derived from the original polymer. ^e Radical polymerization: initiator (*iso*-PrOCOO)₂, $[\text{M}]/[\text{I}] = 50$, time 24 hours.

2(b). The tacticity was changed to atactic ($m:r = 50:50$), and the intensity of the α -methine signal decreased due to hydrogen-deuterium exchange. These results clearly indicate that racemization of the main chain occurred.

Figure 3(a) depicts the ^1H NMR spectrum of the mixture of poly(DPAA) (entry 3 in Table II), measured at 90°C after heating in $\text{D}_2\text{SO}_4/\text{CD}_3\text{OD}$ (60:40) at 90°C for 11 hours. No decrease in the intensity of the α -methine proton was observed, indicating that no

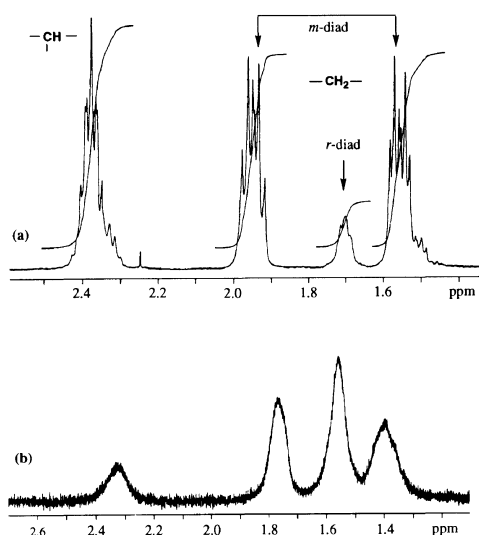


Figure 2. 500 MHz ^1H NMR spectra of poly(methyl acrylate) obtained by anionic polymerization in toluene using *n*-BuLi (a) in chloroform-*d* 60°C and (b) after heating for 1 hour at 90°C in sulfuric acid-*d*₂ and deuterium oxide (90:10).

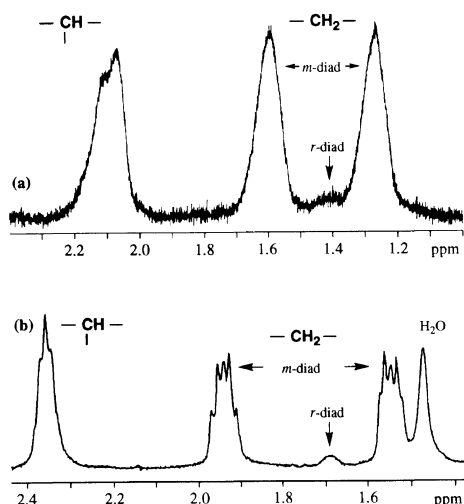


Figure 3. 500 MHz ^1H NMR spectra of (a) a reaction mixture of poly(DPAA) after heating for 11 hours at 90°C in sulfuric acid-*d*₂ and methanol-*d*₄ (60:40), and (b) poly(MA) derived from the same poly(DPAA) by heating for 3 days at 90°C in sulfuric acid and methanol (60:40) (spectrum was measured in chloroform-*d* at 60°C).

deuterium substitution or racemization took place under this condition. When the ^1H NMR spectrum of poly(MA) with 95% *meso* was measured in $\text{D}_2\text{SO}_4/\text{CD}_3\text{OD}$ (60:40), the spectral pattern was similar to Figure 3(a), suggesting that poly(MA) is directly derived from poly(DPAA) in a mixture of sulfuric acid and methanol. Further, Figure 3(b) shows the ^1H NMR spectrum of the poly(MA), derived from poly(DPAA) by the treatment with sulfuric acid-methanol (60:40) at 90°C for 3 days followed by methylation with diazomethane. Diad tacticity was estimated to be 95% *meso* (entry 3 in Table II).

The poly(DPAA) prepared by *n*-BuLi in THF at -98°C (entry 7 in Table II) and poly(MA) derived from it under the above condition with sulfuric acid and methanol (60:40) were analyzed by GPC (Figure 4). The pattern of the poly(DPAA) is quite similar to that of the poly(MA). This indicates that no decomposition

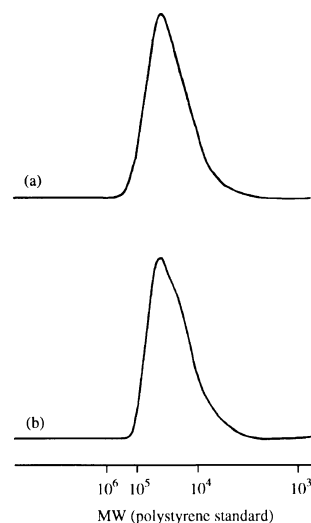


Figure 4. GPC traces of (a) poly(DPAA) (entry 8 in Table II), and (b) poly(MA) derived from the poly(DPAA).

of the polymer main chain occurred during the transformation.

Stereospecific Polymerization of DPAA

According to the above procedure, the diad stereoregularity of poly(DPAA)s obtained by anionic polymerization with *n*-BuLi was estimated, and the results are summarized in Table II. When toluene was used as solvent in the anionic polymerization (entry 1–3), the polymerization proceeded in good yields and the obtained polymers were insoluble in common organic solvents such as chloroform or THF, probably because of a high stereoregularity. Though the degree of polymerization (DP) and molecular weight distribution (M_w/M_n) of the polymer were greatly affected by polymerization temperature, tacticity was not changed by temperature, and rich in a *meso* diad (94–95%). However, the polymerization in THF afforded a polymer rich in a *racemo* diad (entry 4–8) which is soluble in THF or chloroform. Syndiotacticity increased with decreasing polymerization temperature, and changed from $r=53\%$ at 0°C to $r=66\%$ at -110°C . The most syndiotactic polymer ($r=85\%$) was obtained in the radical polymerization using perloyl as the initiator in toluene (entry 9).

In Table III are shown the results of the polymerization of DPAA in toluene or THF using *t*-BuLi or *t*-BuMgBr at low temperature. Polymerization using *t*-BuMgBr gave the polymer in low to moderate yields. An isotactic polymer ($m=80\%$) was obtained in toluene, while syndiotactic rich polymers were produced in THF. General features of the stereospecific polymerization of DPAA seem similar to those of methyl methacrylate⁹ and methyl acrylate.¹⁰

The stereoregularity of the polymers obtained by asymmetric anionic polymerization of DPAA in toluene using the complex of (–)-sparteine and fluorenyllithium was also investigated.³ The results are summarized in Table IV. The stereoregularity of the polymers obtained by asymmetric anionic polymerization was rich in *meso* diad (64–88%), and the polymer with higher specific optical rotation showed higher isotacticity. Optically active poly(DPAA) with the highest isotacticity ($m=$

Table III. Anionic polymerization of DPAA using *t*-BuLi or *t*-BuMgBr^a

Entry	Initiator	Solvent	Temp/°C	Yield/% ^b	DP ^c	\bar{M}_w/\bar{M}_n^c	Tacticity ^d (<i>m</i> : <i>r</i>)
1	<i>t</i> -BuLi	Toluene	-78	94	745	9.39	87:13
2	<i>t</i> -BuLi	Toluene	-98	92	611	4.54	94:6
3	<i>t</i> -BuLi	THF	-78	95	103	1.32	40:60
4	<i>t</i> -BuLi	THF	-98	91	106	1.28	38:62
5	<i>t</i> -BuLi	THF	-110	90	91	1.19	35:65
6	<i>t</i> -BuMgBr	Toluene	-78	48	58	1.13	80:20
7	<i>t</i> -BuMgBr	THF	-78	87	86	1.15	43:57
8	<i>t</i> -BuMgBr	THF	-98	43	51	1.75	40:60
9	<i>t</i> -BuMgBr	THF	-110	0.5	—	—	—

^a [M]/[I] = 20, time 2 hours. ^b Methanol insoluble part. ^c Determined by GPC using poly(methyl acrylate) derived from the original polymer and polystyrene standards. ^d Determined by ¹H NMR using poly(methyl acrylate) derived from the original polymers.

Table IV. Tacticity of the polymer obtained by asymmetric anionic polymerization of DPAA in toluene using (-)-sparteine-fluorenyllithium complex as initiator.^a

Entry	Temp/°C	Time	Yield/% ^b	\bar{M}_n^c	\bar{M}_w/\bar{M}_n^c	$[\alpha]_D^{25}$ ^d		Tacticity ^e (<i>m</i> : <i>r</i>)
						589 nm	365 nm	
1	-78	1 h	91	4200	1.16	-32°	-201°	64:36
2	-98	2 h	93	4700	1.25	-34°	-249°	74:26
3	-98	6 sec.	31	3700	1.10	-48°	-352°	88:12

^a [M]/[I] = 20. ^b Methanol insoluble part. ^c Determined by GPC, polystyrene standards. ^d Measured in CHCl₃-CF₃CO₂H, *c* 0.5. ^e Determined by ¹H NMR using poly(methyl acrylate) derived from the original polymer.

88%) was obtained as entry 3.

In conclusion, we have established a method for transforming poly(DPAA) to poly(MA) without racemization. The transformation was performed by solvolysis of poly(DPAA) in a 60:40 volumetric mixture of sulfuric acid and methanol at 90°C for 24 hours. By this method, diad tacticity of the polymer was able to be determined by ¹H NMR spectroscopy. A highly isotactic polymer (*m* = 95%) was obtained by anionic polymerization with alkylolithiums or *t*-BuMgBr in toluene at low temperature and syndiotactic rich polymer in THF. Most syndiotactic polymer (*r* = 85%) was produced by radical polymerization. In asymmetric anionic polymerization using (-)-sparteine-fluorenyllithium complex, the content of isotactic (*meso*) diad increase with specific optical rotation (*m* = 88%, $[\alpha]_{365} = -352^\circ$).

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