The Effect of the *N*-Substituent *s-trans* to the Carbonyl Group of *N*-Methylacrylamide Derivatives on the Stereospecificity of Radical Polymerizations

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ABSTRACT: Radical polymerization of *N*-methylacrylamide (NMAAm), *N*,*N*-dimethylacrylamide (DMAAm), and *N*-methyl-*N*-phenylacrylamide (MPhAAm) was investigated in toluene at low temperatures. Atactic, isotactic, and syndiotactic polymers were obtained by the polymerization of NMAAm, DMAAm, and MPhAAm, respectively, indicating that the stereospecificity of the radical polymerization of acrylamide derivatives depended on the *N*-substituents of the monomer used. From the viewpoint of monomer structure, the origin of the stereospecificity of radical polymerization of NMAAm derivatives is discussed.

Keywords: radical polymerization; stereospecific polymerization; isotactic; syndiotactic; *N*-methyl-*N*-phenylacrylamide; monomer conformation;

INTRODUCTION

Stereospecific radical polymerization is a challenging topic in polymer synthesis and has attracted much attention. In particular in the last decade, stereoregulation of radical polymerization has been reported for a wide range of monomers.[1-24] It has been revealed that stereospecificity of radical polymerization is determined by a combination of several factors such as monomer structure, concentration, solvent, temperature, complexation, and template effects.

Radical polymerization of *N*,*N*-disubstituted acrylamides is one of the representative systems in which stereospecificity depends on monomer structure.[4] *N*,*N*-Dimethylacrylamide (DMAAm) tends to afford isotactic polymer, in particular in non-polar solvents such as toluene at low temperatures, whereas *N*,*N*-diphenylacrylamide (DPhAAm) gives syndiotactic polymer regardless of the solvents and temperature.

Recently, we have reported that hydrogen bonding interactions are useful for controlling the stereospecificity of the radical polymerization of acrylamide derivatives. In the course of that study,[11-16,18] it was found that the *N*-substituent *s-trans* to the carbonyl group of *N*-methylacrylamide (NMAAm) derivatives plays an important role in determination of stereospecificity of their radical polymerizations. In this paper, the mechanism of radical polymerization of NMAAm derivatives is discussed, based on the polymerization results and the monomer structures.

EXPERIMENTAL

Materials

N-Methyl-*N*-phenylacrylamide (MPhAAm) was prepared according to literature methods.[25] Toluene was purified by washing with sulfuric acid, water and 5% aqueous NaOH, followed by fractional distillation. Tri-*n*-butylborane (*n*-Bu_3B), purchased as a tetrahydrofuran (THF) solution (1.0 M) (Aldrich Chemical Co.), was used without further purification.

Polymerization

A typical polymerization procedure was as follows. MPhAAm (0.426 g, 2.64 mmol) was diluted with toluene to a total volume of 5 mL giving a final concentration of 0.528 mol L^{-1}. 4 mL of this solution was transferred to a glass ampoule and cooled to 0°C. Polymerization was initiated by adding an aliquot of *n*-Bu_3B solution (0.21 mL, 1.0 M) to the monomer solution.[26] After 24 h, the reaction was terminated by adding 2,6-di-*t*-butyl-4-methylphenol in THF (0.5 mL, 1.0 M) at the polymerization temperature. The polymerization mixture was poured into methanol (150 mL). The polymer precipitated was collected by filtration or centrifugation, and dried *in vacuo*. The polymer yield was determined gravimetrically.

Measurements

400 MHz ^{1}H NMR spectra were obtained using an EX-400 spectrometer (JEOL Ltd.). The tacticity of the polymers obtained was determined from the ^{1}H NMR signals of the

methylene groups in the main chain, in deuterated dimethyl sulfoxide (DMSO-d_6) at 150°C. The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC), using polystyrene samples as molecular weight standards. SEC was performed with an HLC 8220 chromatograph (Tosoh Co.) equipped with TSK gel columns (SuperHM-M (6.5 mm ID × 150 mm) and SuperHM-H (6.5 mm ID × 150 mm), Tosoh Co.). Dimethylformamide containing LiBr (10 mmol L^{-1}) was used as eluent at 40°C with flow rate 0.35 mL min^{-1}. The initial polymer concentration was 1.0 mg mL^{-1}.

RESULTS AND DISCUSSION

Radical Polymerization of NMAAm Derivatives in Toluene at Low Temperatures

The radical polymerization of NMAAm, DMAAm, and MPhAAm was carried out in toluene at low temperatures (Table 1). Stereoregularity of the polymers obtained varied widely with the *N*-substituents of the monomer used. Figure 1 shows relationships between the polymerization temperature and the *r* dyad content of the polymers obtained. NMAAm, a monosubstituted acrylamide, gave atactic polymers regardless of the temperature, whereas DMAAm and MPhAAm, disubstituted acrylamides, provided polymers rich in *m* and *r* dyads, respectively. These results suggest that the second *N*-substituent on the NMAAm derivatives plays an important role in inducing stereospecificity of their radical polymerizations. It has previously been shown that the radical polymerization of DPhAAm produces syndiotactic polymers.[4] This means that the stereospecificity of radical polymerization of *N*,*N*-disubstituted acrylamides changes

from isotactic to syndiotactic when at least one of the two *N*-methyl groups in DMAAm is replaced by a phenyl group.

<Table 1>

<Figure 1>

Figure 2 shows the relationship between the stereospecificity of radical polymerization and the structure of the monomer. Monosubstituted acrylamides favor the *s-trans* O=C-N-H conformation.[27] *N*-Aryl-*N*-methylamides favor the *s-trans* O=C-N-Ar conformation, in which the aryl group is perpendicular to the planar amide group.[25,28] Thus, the structure of the *N*-substituent *s-trans* to the carbonyl group appears to determine the stereospecificity of radical polymerization of NMAAm derivatives.

<Figure 2>

The differences in activation enthalpy ($\Delta H_i^{\ddagger}-\Delta H_s^{\ddagger}$) and activation entropy ($\Delta S_i^{\ddagger}-\Delta S_s^{\ddagger}$) between isotactic and syndiotactic propagations for NMAAm, DMAAm and MPhAAm polymerizations in toluene are summarized in Table 2.[29] It should be noted that the absolute value of $\Delta S_i^{\ddagger}-\Delta S_s^{\ddagger}$ for MPhAAm polymerization was small, whereas the absolute values of both $\Delta H_i^{\ddagger}-\Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger}-\Delta S_s^{\ddagger}$ increased significantly for DMAAm polymerization. This means that the difference in degree of freedom between isotactic and syndiotactic propagations is quite small for the polymerization of MPhAAm as

compared to the polymerization of DMAAm.

<Table 2>

The Role of the *N*-Substituent *s-trans* to the Carbonyl Group of NMAAm Derivatives in Stereospecificity of Radical Polymerization

In the radical polymerization of NMAAm derivatives, the incoming monomer will approach the propagating radical center, as shown in Scheme 1, in a way which reduces the steric repulsion between the amide moieties of the monomer and the propagating chain-end. When NMAAm is used as the monomer, the chain end of the newly formed radical (**A**) is free to rotate, as there is little steric hindrance. The freely rotating radical (**B**) can react with a new incoming monomer via two possible pathways, pathway **a** forming an *r* dyad and pathway **b** an *m* dyad. As the chain end rotates, neither pathway is favored and are equally likely, resulting in the formation of an atactic polymer.

<Scheme 1>

In DMAAm polymerization, the chain end of the newly formed radical (**A**) can rotate as in the NMAAm polymerization. However, the radical adopts a different conformation due to steric repulsion between the second methyl groups *s-trans* to the carbonyl groups on the monomeric units near the chain end. This conformationally rotated radical (**C**) also can react with a new incoming monomer via two possible

pathways. Propagation via pathway **b** will be preferred due to the steric hindrance of the amide moiety at the penultimate monomeric units, resulting in the formation of an isotactic polymer.

In MPhAAm polymerization, the conformation of the chain end of the newly formed radical (**A**) will be rotated due to the steric repulsion between the amide moieties at the monomeric units near the chain end. However, to keep the phenyl and amide groups perpendicular at the antepenultimate and penultimate monomeric units, the radical **A** will not be able to rotate near the chain end. This conformationally constrained radical (**D**) also can react with a new incoming monomer via two possible pathways. The steric hindrance of the amide moiety at the penultimate monomeric unit would prevent the approach via this side reducing reaction via pathway **b**, resulting in the formation of a syndiotactic polymer. The small absolute value of $\Delta S_i^{\ddagger}-\Delta S_s^{\ddagger}$ for MPhAAm polymerization would reflect such constraint of conformation near the propagating chain-end.

CONCLUSION

The radical polymerization of NMAAm derivatives was investigated in toluene at low temperatures. It was revealed that NMAAm, DMAAm, and MPhAAm gave atactic, isotactic, and syndiotactic polymers, respectively. From the viewpoint of monomer structure, it was suggested that the *N*-substituent *s-trans* to carbonyl group is an important factor in the stereospecificity of the radical polymerization of NMAAm derivatives. Application of this result to the prediction of stereospecificity of radical polymerization

of other acrylamide derivatives is ongoing.

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Table 1. Radical Polymerization of NMAAm, DMAAm, and MPhAAm in Toluene at Low Temperatures for 24 h[a]

Run	Monomer	Temp.	Yield	Dyad / %[b]		M_n[c]	M_w/M_n[c]
		°C	%	*m*	*r*	x 10^4	
1[d,e]	NMAAm	0	>99	49	51	nd	nd
2[d,e]	NMAAm	–20	>99	49	51	nd	nd
3[d,e]	NMAAm	–40	85	50	50	nd	nd
4[d,e]	NMAAm	–60	76	51	49	nd	nd
5[d,e]	NMAAm	–80	>99	52	48	nd	nd
6[f]	DMAAm	0	82	62	38	1.21	1.5
7[f]	DMAAm	–20	77	64	36	1.39	1.5
8[f]	DMAAm	–40	41	66	34	1.50	1.6
9[f]	DMAAm	–60	56	70	30	2.21	1.6
10[f]	DMAAm	–80	62	73	27	5.20	1.8
11	MPhAAm	0	77	30	70	3.14	1.5
12	MPhAAm	–20	87	28	72	3.78	1.6
13	MPhAAm	–40	89	26	74	4.13	1.5
14	MPhAAm	–60	86	25	75	4.40	1.5
15	MPhAAm	–80	26	24	76	3.72	1.3

a. $[\text{Monomer}]_0$=0.5 mol L^{-1}, $[n\text{-}Bu_3B]_0$=0.05 mol L^{-1}.

b. Determined by ^1H NMR signals due to methylene group.

c. Determined by SEC (polystyrene standards).

d. Monomer, polymer or both were precipitated during polymerization reaction.

e. Data from ref. 15.

f. Data from ref. 18b.

Table 2. Activation Parameters for the Radical Polymerization of NMAAm, DMAAm or MPhAAm in toluene

Monomer	$\Delta H_i^{\ddagger}$-$\Delta H_s^{\ddagger}$ kJ mol^{-1}	$\Delta S_i^{\ddagger}$-$\Delta S_s^{\ddagger}$ J mol^{-1} K^{-1}
NMAAm	0.71±0.07	–3.0±0.3
DMAAm[a]	–2.84±0.14	9.5±0.6
MPhAAm	1.64±0.25	–1.3±1.1

a. Data from ref. 18b.

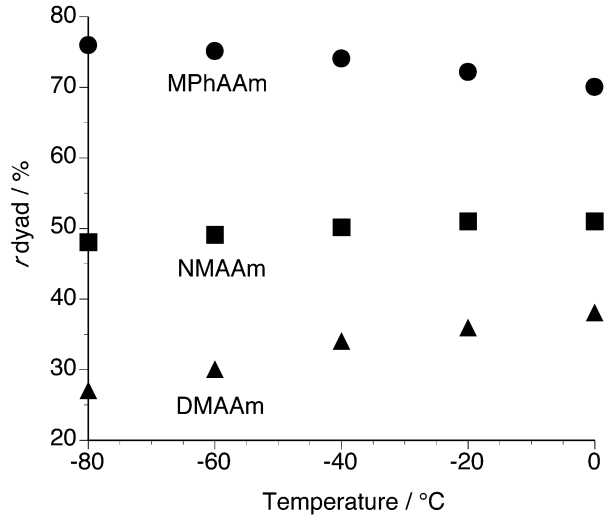
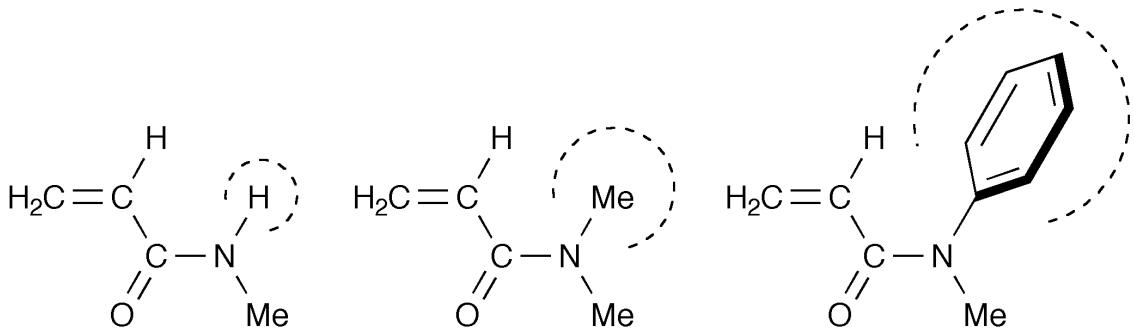
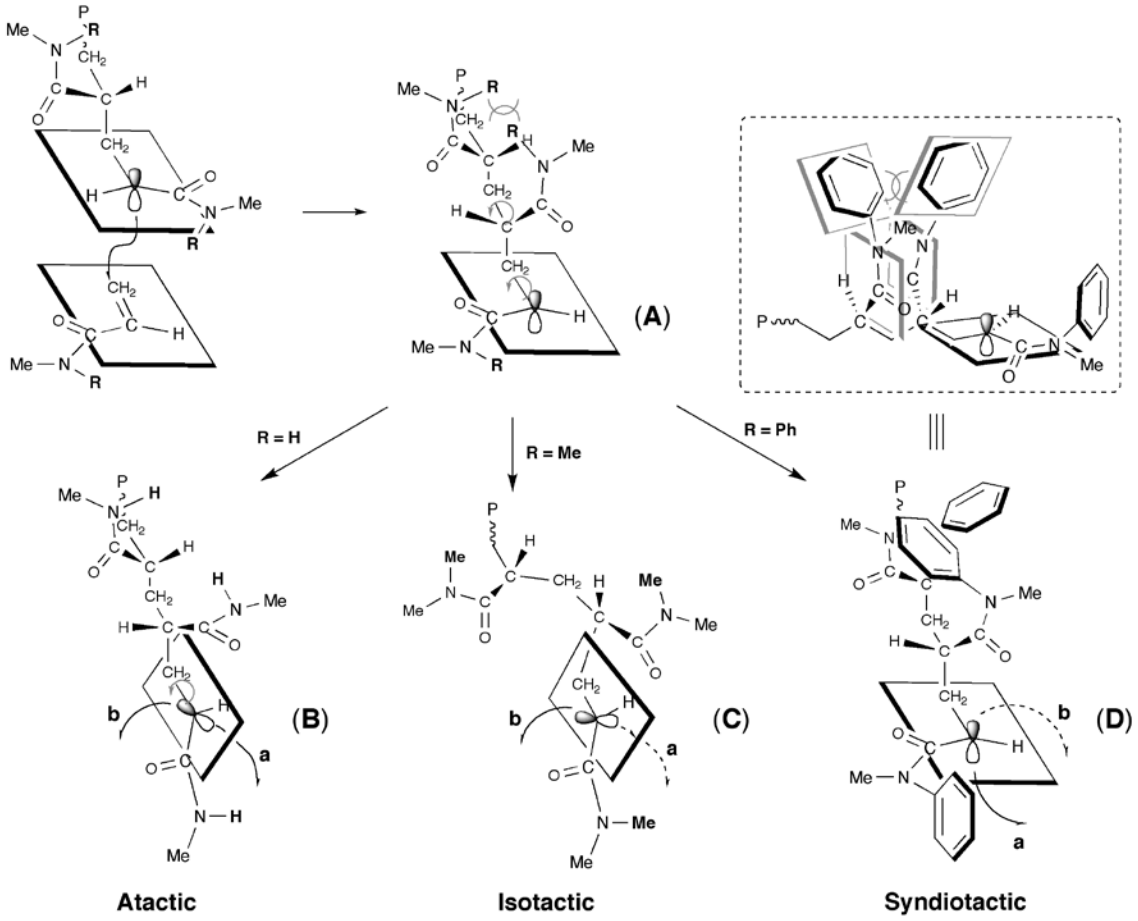


Figure 1. Relationship between the polymerization temperature and *r* dyad content of polymers prepared by radical polymerization of NMAAm, DMAAm or MPhAAm in toluene at low temperatures.



Atactic **Isotactic** **Syndiotactic**

Figure 2. Relationship between the *N*-substituent *s-trans* to carbonyl group in *N*-methylacrylamide derivatives and the stereospecificity of their radical polymerizations.



Scheme 1. Proposed mechanism for the three types of stereospecific radical polymerizations of *N*-methylacrylamide derivatives, in which the *N*-substituent *s-trans* to carbonyl group plays an important role.