

SHORT COMMUNICATIONS

Asymmetric Radical Polymerization of *N*-Phenylmethacrylamides

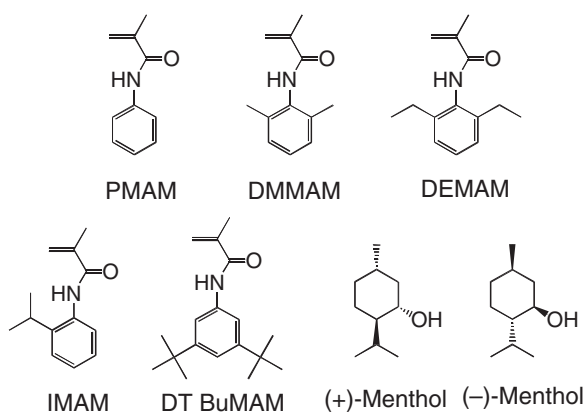
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(Received April 5, 2005; Accepted May 3, 2005; Published August 15, 2005)

KEY WORDS Asymmetric Polymerization / Radical Polymerization / Methacrylamide /
N-Phenylmethacrylamide /
[DOI 10.1295/polymj.37.629]

Triarylmethyl methacrylates, such as triphenylmethyl methacrylate (TrMA), produce a highly isotactic, optically active polymer by the anionic polymerization using chiral initiators.¹ The obtained polymers maintain a single-handed helical conformation in solution due to the steric repulsion of the bulky side groups. Furthermore, the radical polymerization of a TrMA analogue, 1-phenyldizenzosuberyl methacrylate, under chiral conditions also produces a stable helical polymer.² The helical polymers have been utilized as a chiral adsorbent³ and a ligand.⁴ Recently, we found that *N*-triphenylmethylmethacrylamide (TrMAM) and *N*-(4,4'-dibutyl)triphenylmethylmethacrylamide can also produce highly isotactic, optically active polymers *via* the radical polymerization under chiral conditions.⁵



In the present study, in order to obtain the optically active polymers with a chiral structure, the asymmetric radical polymerizations of *N*-phenylmethacrylamide (PMAM) and its derivatives bearing various substituents on the phenyl group, *N*-(2,6-diethylphenyl)methacrylamide (DEMAM), *N*-(2,6-dimethylphenyl)methacrylamide (DMMAM), *N*-(2-isopropylphenyl)methacrylamide (IPMAM), and *N*-(3,5-di-*tert*-

butylphenyl)methacrylamide (DTBMAM), were carried out in optically active solvents, *i.e.*, (+)- and (–)-menthol. Among these monomers, only the 2,6-disubstituted derivatives, DEMAM and DMMAM, were found to produce optically active polymers.

EXPERIMENTAL

Synthesis of Monomers. The *N*-phenylmethacrylamide derivatives were prepared by the reaction of the corresponding anilines and methacryloyl chloride in the presence of triethylamine in chloroform according to previously reported procedures.⁶ The monomers were identified by NMR and elementary analysis. PMAM and DMMAM are known monomers, and DEMAM, IPMAM, and DTBMAM are new monomers to the best of our knowledge.

N-(2,6-Diethylphenyl)methacrylamide (DEMAM). Yield: 47%. Mp: 140.5–141.2 °C. ¹H NMR (CDCl₃): δ 1.20 (t, 3H, ethyl CH₃), 2.09 (m, 3H, allyl CH₃), 2.60 (t, 2H, ethyl CH₂), 5.46 (s, 1H, vinyl), 5.82 (s, 1H, vinyl), 7.04 (s, 1H, –NH), 7.10–7.27 (m, 3H, aromatic). Elemental analysis. Found: C, 77.69%; H, 8.91%, N, 6.34%. Calcd for C₁₄H₁₉NO: C, 77.38%; H, 8.81%; N, 6.45%.

N-(2-Isopropylphenyl)methacrylamide (IPMAM). Yield: 34%. Mp: 69.3–69.7 °C. ¹H NMR (CDCl₃): δ 1.27 (d, 6H, isopropyl CH₃), 2.09 (s, 3H, allyl CH₃), 3.02 (m, 1H, isopropyl CH), 5.47 (s, 1H, vinyl), 5.82 (s, 1H, vinyl), 7.23 (m, 3H, aromatic), 7.43 (s, 1H, –NH), 7.80 (m, 1H, aromatic) ppm. Elemental analysis. Found: C, 76.82%; H, 8.47%; N, 6.93%. Calcd for C₁₃H₁₇NO: C, 76.81%; H, 8.43%; N, 6.89%.

N-(3,5-di-*tert*-Butylphenyl)methacrylamide (DTBMAM). Yield 51%. Mp: 177.9–178.3 °C. Yield: 51%. ¹H NMR (CDCl₃): δ 1.33 (s, 18H, *tert*-butyl CH₃), 2.08 (m, 3H, allyl CH₃), 5.45 (t, 1H, vinyl), 5.79 (s,

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Table I. Radical Polymerization of DEMAM and PMAM at 60 °C^a

Run	Monomer	[M] ₀ (M)	Solvent (v/v)	Yield ^b (%)	M _n ^c (×10 ³)	M _w /M _n ^c
1	PMAM	1.0	THF	92	6.7	2.0
2	PMAM	0.5	(-)-Menthol/Toluene (10/1)	98	29.5	2.4
3	PMAM	0.5	(+)-Menthol/Toluene (10/1)	79	30.4	2.6
4	DEMAM	1.0	THF	34	4.3	1.3
5	DEMAM	0.5	(-)-Menthol/Toluene (10/1)	82	—	—
6	DEMAM	0.5	(+)-Menthol/Toluene (10/1)	84	—	—

^aInitiator = AIBN (0.02 M), time = 24 h. ^bMethanol/H₂O = 3/1-insoluble part. ^cDetermined by SEC (polystyrene standard) in THF at 40 °C.

1H, vinyl), 7.19 (m, 1H, aromatic), 7.42 (m, 2H, aromatic), 7.46 (s, 1H, -NH) ppm. Elemental analysis. Found: C, 79.07%; H, 9.82%; N, 5.19%. Calcd for C₁₈H₂₇NO: C, 79.07%; H, 9.95%; N, 5.12%.

Reagents. α,α' -Azobisisobutyronitrile (AIBN; Kishida; purity > 99%) was purified by recrystallization from methanol. The chiral additives, (+)-neomenthol (TCI; >96%) and (-)-menthone (Aldrich; 90%), were used after being distilled from CaH₂ under reduced pressure. The dry solvents, THF and toluene (Kanto Kagaku), and chiral solvents (additives), (-)- and (+)-menthols (Kishida; 99%, TCI; >99%), (+)-isomenthol (Aldrich; 99%), dihydrocholesterol (Sigma; 95%) and (+)-dimethyl tartarate (Aldrich; 99%) were used for the polymerization without further purification.

Polymerization. The radical polymerization was carried out under dry nitrogen in a glass ampule equipped with a three-way stopcock using AIBN as the initiator. The reaction products were precipitated in a large excess of methanol or methanol-water, and were isolated using a centrifuge. The absence of menthol in the obtained polymers was confirmed by the IR in the solid state and the ¹H NMR of the polymer solution in D₂SO₄.

CD Measurements in Solid States. The polymers were dispersed in liquid paraffin as a small particle after grinding in a mortar, and interposed between quartz plates.⁷ The CD spectra were measured at almost the same concentrations and UV intensities for each sample.

Measurements. The ¹³C NMR spectra were measured using a Varian Gemini 2000 spectrometer (400 MHz for ¹H). The tacticity of poly(PMAM) was determined from the NMR peaks of the α -methyl carbon in DMSO-*d*₆ at 80 °C. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were determined by size exclusion chromatography (SEC) calibrated with standard polystyrenes using a Jasco PU-980 pump equipped with a Jasco RI-930 detector and a set of TSKgel GMH_H-H and G3000_H columns (with THF as an eluent) at 40 °C. The circu-

lar dichroism (CD) spectra were obtained using a Jasco J-720L apparatus. The IR spectra were measured using a Jasco FT/IR-620 spectrometer.

RESULTS AND DISCUSSION

The radical polymerizations of PMAM and DEMAM were carried out in THF and a menthol/toluene (10/1) mixture, and the results are shown in Table I. The polymerization of PMAM produced soluble polymers in good yields, while the polymerization of DEMAM in THF afforded a soluble polymer in a lower yield, while the polymer produced during the polymerization in a menthol/toluene mixture was insoluble in common solvents including THF and chloroform. However, the polymer was dissolved in sulfuric acid. The poly(PMAM)s obtained from menthol/toluene mixtures had a higher M_n than that from THF. The higher molecular weight may be associated with the lower chain-transfer to this solvent. The poly(DEMAM) obtained in the menthols may also have a higher molecular weight, which would be another reason for the lower solubility.

The poly(PMAM)s had the same stereoregularity (mm/mr/rr = 8/39/53) regardless of the polymerization solvents. Although the NMR spectra of the poly(DEMAM)s showed no clear information on the stereoregularity, the polymer obtained in the menthols may have a higher regularity, which would also be another reason for low solubility.

The polymers dissolved in a solvent were optically inactive, and exhibited no circular dichroism (CD) adsorption. The CD measurement was also conducted for the polymer samples dispersed in liquid paraffin (nujol) (Figure 1).⁷ The poly(DMAM)s and the poly(DEMAM) obtained from THF exhibited no CD peaks. However, clear CD peaks were observed for the poly(DEMAM)s obtained from the (+)- and (-)-menthol/toluene solvents. The CD patterns of the polymers were the mirror images of each other. These results indicate that a stable chiral conformation is constructed during the polymerization of DEMAM

Table II. Radical polymerizations of DMMAM, IMAM, and DTBMAM in THF and (–)-menthol^a

Run	Monomer	Temp. (°C)	Solvent (v/v)	Yield ^b (%)	M_n^c ($\times 10^3$)	M_w/M_n^c
1	DMMAM	60	THF	20	4.49	1.6
2	DMMAM	60	(–)-Menthol/Toluene (5/2)	90		
3	IMAM	60	(–)-Menthol/Toluene (5/2)	99	29.3	7.6
4	DTBMAM	20	(–)-Menthol/Toluene/CHCl ₃ (22/11/10)	39	3.0	2.3

^a[M]₀ = 0.5 M, initiator = AIBN (0.02 M), time = 24 h. ^bMethanol-insoluble part. ^cDetermined by SEC in THF at 40 °C.

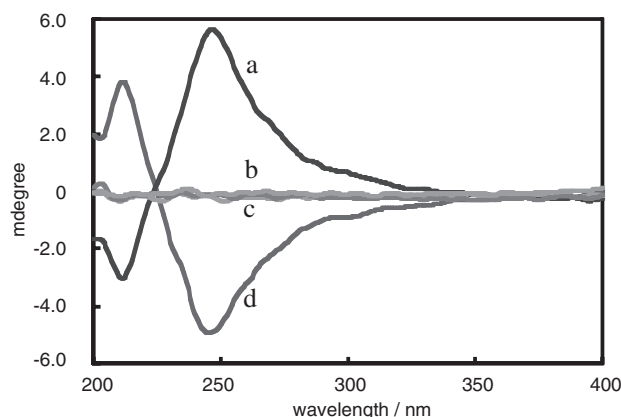


Figure 1. CD spectra of poly(DEMAM) (a: obtained in (–)-menthol, c: in THF, and d: in (+)-menthol) and poly(PMAM) (b: obtained in (–)-menthol) (Samples were dispersed in liquid paraffin for CD measurement).

in the optically active solvents, although such a conformation was not formed for PMAM. The CD pattern did not change even after heating for 3 h at 60 °C.

The radical polymerizations of *N*-(2,6-dimethylphenyl)methacrylamide (DMMAM), *N*-(2-isopropylphenyl)methacrylamide (IPMAM), and *N*-(3,5-di-*tert*-butylphenyl) methacrylamide (DTBMAM) were carried out in THF and a (–)-menthol/toluene (5/2) mixture at 60 °C (Table II). The polymerization of DTBMAM had to be carried out in a mixture of (–)-menthol/toluene/CHCl₃ (22/11/10) due to low solubility of the monomer. The results of the polymerization of DMMAM were similar to those of DEMAM and the polymer obtained from THF was soluble in THF and chloroform, but the polymer obtained from the (–)-menthol/toluene mixture was not. Among the three polymers, only poly(DMMAM) showed the CD peaks similar to that of poly(DEMAM) dispersed in nujol while the other two polymers showed no CD peaks. These results indicate that the formation of a chiral conformation is possible only for the *N*-phenylmethacrylamides bearing the substituents at both the 2- and 6-positions.

Figure 2 shows the CD spectra of poly(DEMAM)s prepared at various temperatures in menthol. The melting point of (+)- and (–)-menthol is 43 °C, but

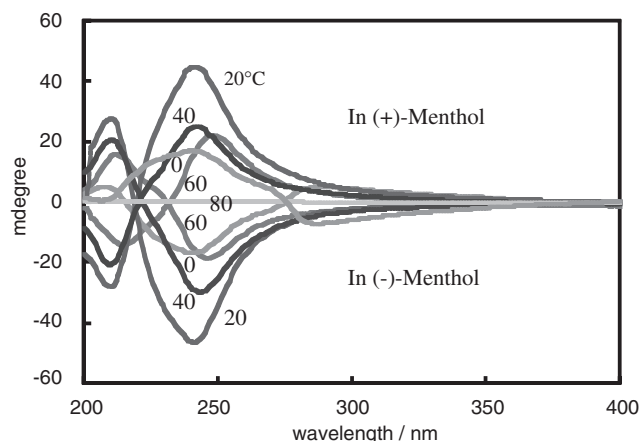


Figure 2. CD spectra of poly(DEMAM)s obtained at 0, 20, 40, 60, and 80 °C in menthol/toluene (5/2) mixture. (Samples were dispersed in liquid paraffin).

even at 0 °C, the mixture of menthol, DEMAM, and initiator was homogeneous, which was maintained during the initial stage of the polymerization. The poly(DEMAM)s obtained at 20 °C showed the highest CD intensity. Poly(DEMAM) was obtained in a low yield (19%) at 80 °C and showed no CD peaks. The peaks in the CD spectra shifted to long wavelength with an increase in the polymerization temperature. The poly(DEMAM)s obtained at 0 °C showed a CD pattern different from the others. The polymer may have a different conformation or tacticity.

The CD spectra of poly(DEMAM) obtained in (–)-menthol at 20 °C were measured in the solid state in nujol after heating at 60, 100, 150, 180, and 200 °C for 3 h (Figure 3). No change in the CD pattern was observed during the heat treatment at 60 °C, but the CD intensity sharply increased by heating at 100 and 150 °C. The poly(DEMAM) may take a more regular structure, probably on the side chain arrangement, by this treatment. However, when the heat treatment was carried out at 180 °C, the CD intensity fairly decreased, and at 200 °C, it completely disappeared. The polymer lost its chiral structure at these temperatures, which are close to the glass transition temperature (194.6 °C) of the poly(DEMAM) obtained at 20 °C.

Although we obtained the optically active polymers

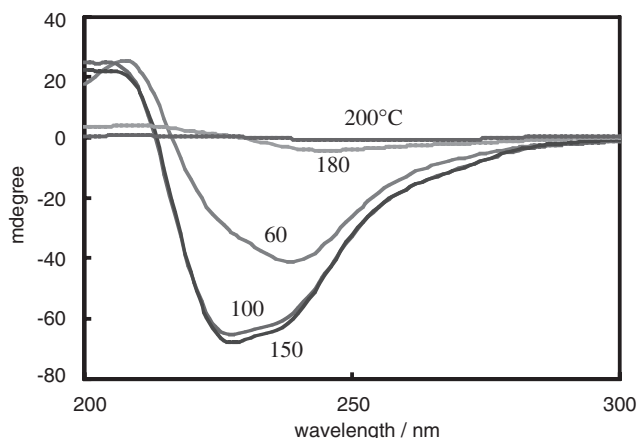


Figure 3. CD spectra of poly(DEMAM) (polymer obtained in (–)-menthol/toluene (5/2) at 20 °C) after heat treatment for 3 h at 60, 100, 150, 180, and 200 °C (Samples were dispersed in liquid paraffin).

from the 2,6-disubstituted *N*-phenylmethacrylamides, the reason for the formation of these polymers is not clear. One of the possible reasons may be as follows. The methacrylamide monomers can form specific complexes with the chiral menthol through hydrogen bonding. This chiral complex may affect the stereochemistry of the monomer addition to a growing radical, and the resulting polymer may have a chiral conformation, which can be maintained even after the completion of the chain growth, due to the steric hindrance of the substituents introduced on the 2 and 6 positions. The induction of the chirality seems to be more efficiently attained at a lower temperature. The polymers without the two substituents cannot form a stable chiral conformation and are more soluble. The optically active polymers may show a chiral recognition as well as other optically active polymethacrylamides.⁸

CONCLUSIONS

We, for the first time, succeeded in obtaining opti-

cally active polymers through the asymmetric radical polymerizations of 2,6-disubstituted *N*-phenylmethacrylamide derivatives in optically active solvents, such as (+)- and (–)-menthol. The polymers were not soluble in organic solvents, but clearly showed CD peaks when dispersed in liquid paraffin. However, the poly(*N*-phenylmethacrylamide)s prepared from the monomers without two substituents at both the 2- and 6-positions exhibited no CD absorption in the solid state. The chiral structure is constructed only from the 2,6-disubstituted *N*-phenylmethacrylamides and is stably maintained in the solid state even at rather high temperatures.

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