Helix-Sense-Selective Free Radical Polymerization of *N*-(Triphenylmethyl)methacrylamide Derivatives

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ABSTRACT: Two novel monomers, *N*-[(±)-(2-fluorophenyl)(4-fluorophenyl)(phenyl)methyl]methacrylamide (2F4FPhMAM) and *N*-[(4-butyl)triphenylmethyl]methacrylamide (BuTrMAM), were synthesized and polymerized in the presence of (+)- and (−)-menthol as the chiral additive at different temperatures. The obtained polymers, P2F4FPhMAM and PBuTrMAM, are optically active. P2F4FPhMAM is not soluble in common organic solvents and no enantiomer selection was observed in the polymerization of racemic 2F4FPhMAM in the presence of the optically active additive (+)- and (−)-menthols. PBuTrMAM is soluble in THF and chloroform. The circular dichroism spectra of the polymers is similar to that of optically active poly[(triphenylmethyl)methacrylamide] with a prevailing one-handed helicity, suggesting that the present polymers also have a prevailing one-handed helicity. The tacticity of the polymers was estimated from the ^{1}H NMR spectrum of polymethacrylamide derived in D_2SO_4. The polymers are almost 100% isotactic. The chiroptical properties of the obtained polymers were studied in detail.
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Optically active polymers, especially helical polymers, play an important role in the field of polymer science as they have a wide variety of potential applications based on a chiral structure, such as chiral recognition toward racemic compounds and liquid crystal formation.[1–8] Many stereoregular polymers are known to have a helical conformation in the solid state, which may be maintained even in solution if the side chain is very bulky. The optical activity of these polymers is mainly based on a single-handed helical conformation of the main chain which is maintained by steric repulsion between the bulky side groups. Recently, we found that Lewis acids such as rare earth metal triflates significantly increase the isotactic specificity during the radical polymerization of acrylamide and methacrylamide derivatives.[9–12] The radical polymerization of the methacrylates with a bulky side group, such as triphenylmethyl methacrylate (TrMA)[13] and 1-phenyldibenzosuberyl methacrylate (PDBSMA)[14] proceeds in an isotactic-specific manner due to the steric repulsion among the bulky side groups. The helix-sense-selective polymerization of PDBSMA through free radical mechanism gives rise to an optically active, helical polymer having an excessive single-handed helicity from a achiral monomer.[14] This insisted us to study bulky methacrylamides, *N*-(triphenylmethyl)-methacrylamide (TrMAM) and its derivative, *N*-[(4,4′-dibutyl)triphenylmethyl]methacrylamide (DBuTrMAM).[15] The polymers (PDBuTrMAM) prepared by the polymerization of DBuTrMAM in (+)- and (−)-menthol were optically active, and their optical rotation was opposite to that of menthol. This suggests that the optical rotation may not due to the incorporation of menthol residue in the polymer. The CD intensity of the PDBuTrMAM was lower than that of the anionically polymerized one-handed helical poly-(TrMA) with a specific rotation of $[\alpha]_D$ +350°, indicating that the one-handedness of the PDBuTrMAMs may not be high. In the present study, chiral 2F4FPhMAM was synthesized to observe the possibilities of the enantiomer selective polymerization of racemic monomer under chiral condition. To investigate the helix-sense-selective polymerization, BuTrMAM was copolymerized with a small amount of optically active 2F4FPhMAM. BuTrMAM was also polymerized using radical initiators under various conditions, particularly chiral conditions. The polymer (P2F4FPhMAM) prepared from 2F4FPhMAM was not soluble in common organic solvents but PBuTrMAM was soluble in chloroform and THF. The optically active PBuTrMAM exhibited a low chiral recognition. The chiroptical properties of these polymers were also studied in details.

EXPERIMENTAL

Materials

All the reagents used for synthesis of monomers were bought from Aldrich, Kishida, and Kanto Kagaku, and were used without further purification. 2,2′-Azobis-isobutyronitrile (AIBN; Kishida; purity >99%) was purified by recrystallization from methanol. The chiral additives, (+)-neomenthol (TCI; >96%), (R)-(−)-2-octanol (TCI; >98%), (R)-(−)-2-heptanol (Aldrich; >98%), (S)-3-hydroxytetrahydrofurane (TCI; >98%), and (R)-(+)-tetrahydrofuran-2-carboxylic acid (TCI; >98%), were used after being distilled from CaH_2 under a reduced pressure. Dry solvents, THF and toluene (Kanto Kagaku), and the chiral solvents (additives), (−)- and (+)-menthols (Kishida; >99%), were used for polymerization without further purification.

Monomer Synthesis

(±)-2F4FPhMAM

This monomer was synthesized by three steps reaction. Firstly, synthesis of the corresponding alcohol, then the amination of the alcohol, and finally, synthesis of the monomer from the obtained amine.

Synthesis of Alcohol. Phenyl magnesium bromide in diethyl ether was prepared by a conventional method from bromobenzene (43.6 mL, 0.41 mol) and Mg turnings (10.2 g, 0.42 mol). A solution of 2,4′-difluoro-benzophenone (65 g, 0.298 mol) in dry ether (200 mL) was added dropwise to the Grignard reagent, and the reaction was continued for 6 h at room temperature. Then, 400 mL of 3 N aq. HCl was slowly added to the reaction mixture. The aq. solution was neutralized by 4 N aq. NaOH and aq. NH_4Cl. The product was extracted with ether and dried over $MgSO_4$. After the evaporation of the solvent, the obtained alcohol was recrystallized twice from hexane. Yield: 74.4 g (84%), mp 59–60 °C.

Synthesis of Amine from Alcohol. Phosphorus tribromide (5.12 mL, 0.028 mol) was added dropwise to the alcohol (25 g, 0.084 mol) dissolved in diethyl ether (150 mL) at 0 °C. The reaction was continued for 4 h and the solution in a flask turned to brownish color. Then, liquid ammonia was added to the reaction mixture at −78 °C.[16] The organic phase was separated, dried ($MgSO_4$), and evaporated under a reduced pressure. The obtained compound was recrystallized in hexane. Yield: 21.5 g (86.4%), mp 51–52 °C.

Synthesis of (±)-2F4FPhMAM from the Amine. Triethylamine (12.3 mL, 0.088 mol) was added to a chloroform solution of the amine (13 g, 0.044 mol) in a flask. The solution was cooled in an ice water bath and methacryloyl chloride (5 mL, 0.048 mol) was add-

ed dropwise to the flask. The reaction was continued for 2 h at 0 °C and then for 24 h at room temperature, and finally the mixture was refluxed for 1 h. The reaction mixture was washed with saturated aq. $NaHCO_3$ (200 mL) three times and two times with distilled water. The organic phase was separated and dried with $MgSO_4$. After the evaporation of the solvent, the product was recrystallized with hexane and chloroform. Yield: 13.5 g (76%), mp 95 °C.

^{1}H NMR ($CDCl_3$): δ 1.97 (s, 3H, allyl CH_3), 5.36 (s, 1H, vinyl), 5.72 (s, 1H, vinyl), 6.95 (s, 1H, –NH), 7.01–7.29 (m, 13H, aromatic) ppm. Elemental analysis. Found: C, 76.01%; H, 5.27%; N, 3.74%. Calculated for $C_{23}H_{19}F_2NO$: C, 76.02%; H, 5.27%; N, 3.85%.

BuTrMAM

(4-Butyltriphenyl)methanol was synthesized by the Grignard reaction of benzophenone with 4-butylphenylmagnesium bromide in ether. The obtained liquid alcohol was purified by column chromatography (20 g, 75%). From this alcohol, (4-butyltriphenyl-methyl)amine was synthesized with liquid ammonia.[16] The obtained liquid amine was purified by column chromatography (7.3 g, 49%). Finally BuTrMAM was synthesized by the reaction of (4-butyltriphenyl-methyl)amine and methacryloyl chloride in the presence of triethylamine in chloroform in the same way as the synthesis of 2F4FPhMAM. Yield: 8.5 g, (95%).

^{1}H NMR ($CDCl_3$): δ 0.92 (m, 3H, n-butyl CH_3), 1.36 (m, 2H, n-butyl CH_2), 1.56 (m, 2H, n-butyl CH_2), 1.97 (s, 3H, allyl CH_3), 2.58 (t, 2H, n-butyl CH_2), 5.34 (s, 1H, vinyl), 5.7 (s, 1H, vinyl), 6.96 (s, 1H, –NH), 7.09–7.31 (m, 14H, aromatic) ppm. Elemental analysis. Found: C, 84.53%; H, 7.45%; N, 3.66%. Calculated for $C_{27}H_{29}NO$: C, 84.55%; H, 7.62%; N, 3.65%.

Polymerization

The radical polymerization was carried out under dry nitrogen in a glass tube equipped with a three-way stopcock using AIBN as an initiator at 60 °C. The polymerization using AIBN at $-20 \sim 40$ °C was initiated by the irradiation of UV light (400 W high-pressure mercury lamp). Liquid materials were transferred to the glass tube using syringes and the solid monomer using a funnel having a nitrogen gas inlet tube. As BuTrMAM is very reactive, it was preserved as a hexane solution. The BuTrMAM solution was placed in the glass tube and then hexane was evaporated under a reduced pressure at low temperature (0 °C) and a solvent of polymerization was added in it. The solution was maintained at the prescribed temperature for 24 h. The polymerization was terminated by cooling the reaction mixture at −78 °C. The reaction mixture was dissolved in chloroform (5 mL), and the solution was poured into a large

amount of methanol. The precipitated polymers were isolated using a centrifuge, washed several times with methanol to remove the unreacted monomer and the chiral additives, and dried at 60 °C for 10 h. The absence of menthol in the obtained polymers was confirmed by measuring the IR spectra in the solid state and the ^{1}H NMR of the polymer in D_2SO_4.

CD Measurements in a Solid State

The insoluble polymers were dispersed in liquid paraffin by grinding in a mortar, and imposed between quartz plates.[15] The polymer concentrations and the UV intensities of the samples were almost the same for all cases.

Solvolysis of BuTrMAM

The solvolysis reaction of BuTrMAM was carried out in a mixture of $CD_3OD/CDCl_3$ (1/1, v/v) at 35 °C in an NMR tube (Wilmad 507-PP).[17] BuTrMAM (0.15 g, 0.4 mmol) was dissolved in the solvent (1 mL), the tube was placed in a water bath at 35 °C, and reaction was monitored by ^{1}H NMR spectroscopy at 35 °C.

Measurements

The ^{1}H NMR spectra were recorded on a Varian Gemini 2000 spectrometer (400 MHz for ^{1}H). The number average molecular weight (M_n) and polydispersity (M_w/M_n) of the obtained polymers were determined by size-exclusion chromatography (SEC) calibrated using standard polystyrenes on a JASCO PU-980 pump equipped with a JASCO RI-930 detector using TSKgel GMH$_{HR}$-H and G3000$_{HR}$ columns connected in series (eluent THF; temperature 40 °C). The optical rotation was measured in either THF or chloroform at room temperature with a JASCO P-1030 polarimeter. The circular dichroism (CD) spectra were measured with a JASCO J-720L spectrometer.

Resolution of 2F4FPhMAM

The resolution of racemic 2F4FPhMAM was examined using several commercially available chiral HPLC columns, such as CHIRALCEL OD, CHIRALPAK AD, CHIRALCEL OJ, and many other home-made polysaccharide-based chiral columns. Enantiomers were partially resolved (enantiomeric excess 80%), but enantiomeric pure isomers were not obtained.

RESULTS AND DISCUSSION

Radical Polymerization of 2F4FPhMAM

Some methacrylates having bulky side groups afford the prevailing one-handed helical polymers by anionic polymerization using optically active initiators, and even by the radical process in the presence

Table I. Radical polymerization of 2F4FPhMAM[a]

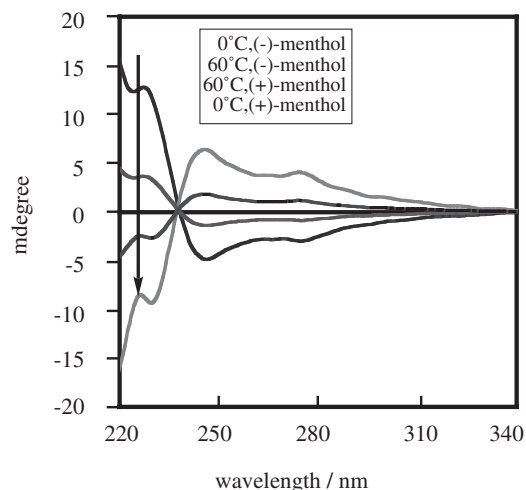| Run	Temp. (°C)	Initiator	Solvent (v/v)	Yield[b] (%)
1	60	AIBN	THF	92
2	60	AIBN	Toluene	90
3	60	AIBN	Toluene/(+)Menthol (5/2)	99
4	60	AIBN	Toluene/(−)Menthol(5/2)	99
5	0	AIBN/UV	Toluene/(+)Menthol (5/2)	75
6	0	AIBN/UV	Toluene/(−)Menthol(5/2)	70

[a]Initiator = AIBN (0.02 M), time = 24 h, $[M]_0 = 0.5$ mol/L.
[b]Methanol-insoluble part.

of optically active additives such as menthol and menthanthiol.[14] The formation of the prevailing one-handed helical polymers by the radical process has been ascribed to the fact that the chain transfer rates of the growing radicals with a right- or left-handed helicity to an optically active transfer agent can be different, and the helical growing polymer with a large transfer constant has a lower chance to propagate to the high molecular weight polymer compared with the opposite helical polymer with a lower transfer constant. Although the radical polymerization of 2F4FPhMAM afforded the polymer in good yields (Table I), the anionic polymerization of this monomer using *n*-BuLi in toluene at −78 °C did not proceed and no polymer was obtained. Usually, acrylamides and methacrylamides with an amide proton cannot be polymerized by the typical anionic process with alkyl lithiums and Grignard reagents.[18]

The radically obtained polymers were insoluble in organic solvents as well as poly(TrMAM).[15] These polymers were dissolved in strong acids, such as concentrated sulfuric acid, accompanying with the cleavage of the bulky side derivative of trityl group to produce polymethacrylamide. The tacticity of the obtained polymers was directly determined from the ^{1}H NMR spectra of the polymethacrylamide derived from the original polymers in D_2SO_4.[15,19] The ^{1}H NMR spectra indicated that the obtained polymers were nearly 100% isotactic similar to poly-(TrMAM).[15] The polymer may be an equimolar mixture of left- and right-handed helices.

Optically active polymers were obtained in the polymerization of racemic 2F4FPhMAM in presence of chiral additive (+)- and (−)-menthol but no enantiomer selection was observed in this process. As P2F4FPhMAMs were insoluble in organic solvents, the CD spectra of these polymers could not be measured in solution, but the spectra were obtained for the polymer particles dispersed in liquid paraffin (Nujol) (Figure 1).[20] The spectral pattern was similar to that of PTrMAM obtained in menthol,[15] and the CD intensity was higher for the polymers prepared at 0 °C.

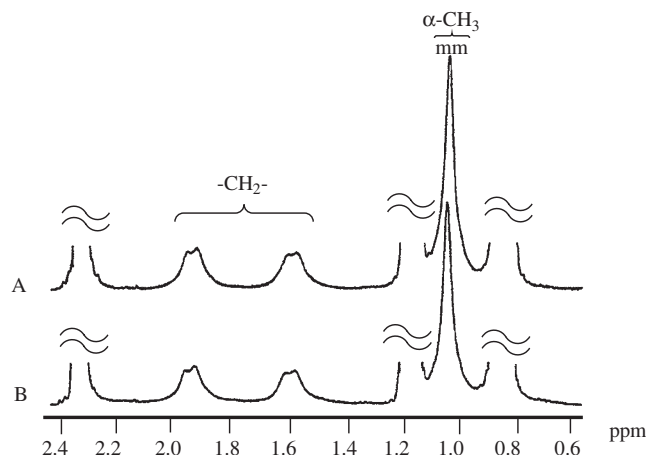**Figure 1.** CD spectra of P2F4FPhMAM in paraffin (run 3 to 6 in Table I) at r.t.

Figure 2. 400 MHz ^{1}H NMR spectra of PMAM (A, derived from PBuTrMAM (run 1 in Table II); B, derived from PBuTrMAM (run 2 in Table II)) (at 60 °C in D_2SO_4). The peaks (0.85, 1.2, 2.35 ppm) are due to the butyl protons on the triphenylmethyl residue of the by-product during sulphuric acid-induced decomposition.

These results support the formation of the prevailing one-handed helical P2F4FPhMAM in menthol.

When BuTrMAM was copolymerized with a small amount of optically active 2F4FPhMAM, the obtained copolymer showed the chiroptical properties, which are expected only from the contribution of 2F4FPhMAM, suggesting that no helix-sense-selective polymerization proceeded.

2F4FPhMAM was not solvolyzed at all in methanol/chloroform (1/1, v/v) at 35 °C even after 10 d, whereas the half-life of TrMA under the same conditions is only 15 min.[21] This indicates that 2F4FPhMAM is much stronger towards hydrolysis and the obtained polymer must be more stable compared with poly(TrMA) when used as a chiral stationary phase in HPLC with polar alcoholic solvents.

Radical Polymerization of BuTrMAM

The radical polymerization of BuTrMAM was carried out in toluene and THF. Although PTrMAM is insoluble in common organic solvents, PBuTrMAM is soluble in chloroform and THF because of the n-butyl group in one of the phenyl group of bulky trityl side chain. The tacticity of the obtained polymer was estimated by the same method as that for P2F4FPhMAM.[15,19] When the PBuTrMAMs (run 1 and 2 in Table II) were dissolved in D_2SO_4, the ^{1}H NMR in Figure 2 shows only one methyl peak due to the isotactic (mm) sequence at 1.05 ppm and two sets of doublet due to the methylene group at 1.60 and 1.95 ppm, indicating that the PBuTrMAMs are highly isotactic. The two ^{1}H NMR spectra are almost identical to each other, which indicates almost no solvent effect on the polymer tacticity.

The polymerization in an optically active medium may helix-sense-selectively proceed because the propagation rates of right- and left-handed helical polymer radicals might be different due to the existence of a chiral substance. The chain transfer to the chiral medi-
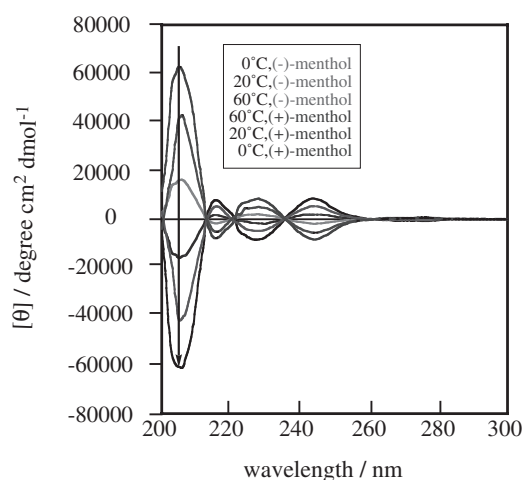
Table II. Radical polymerization of BuTrMAM[a]

Run	Temp. (°C)	Solvent	Yield[b] (%)	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	$[\alpha]_D$[d] (deg)	$[\alpha]_{365}$[d] (deg)
1	60	Toluene	65	2.6	5.2	—	—
2	60	THF	71	1.5	2.1	—	—
3	−20/UV	(+)-Menthol	30	6.1	6.2	−9.4	−28.2
4	−20/UV	(−)-Menthol	27	9.6	5.4	9.5	28.9
5	0/UV	(+)-Menthol	81	30.0	5.3	−9.7	−29.3
6	0/UV	(−)-Menthol	79	29.4	5.3	9.8	29.4
7	20/UV	(+)-Menthol	88	6.4	9.7	−7.0	−21.7
8	20/UV	(−)-Menthol	91	8.2	9.8	6.8	21.8
9	60	(+)-Menthol	90	5.2	3.6	−3.1	−8.8
10	60	(−)-Menthol	84	4.2	3.0	2.9	8.6

[a]Initiator = AIBN (0.02 M), time = 24 h, $[M]_0 = 0.5$ mol/L. [b]Methanol-insoluble part. [c]Determined by SEC in CHCl$_3$ (polystyrene standard) at 40 °C. [d]In CHCl$_3$ at r.t.

um may also be responsible for the helix-sense-selection as described before. Table II shows the results of the radical polymerization of BuTrMAM in (+)- and (−)-menthols. The PBuTrMAMs prepared in (+)- and (−)-menthol were optically active, and their optical rotation was opposite to that of menthol. This suggests that the optical rotation may be not due to the incorporation of the menthol residue in the polymer. The polymerization at 0 °C produced the polymers having a larger specific rotation than that at 20 °C. The optical activity gradually decreased with an increase of the polymerization temperature.

The spectral pattern of PBuTrMAMs is similar to that of the PDBuTrMAM obtained in the same menthol (Figure 3).[15] The CD intensity of the polymer also decreased with an increase in the polymerization temperature. These results support the formation of the prevailing one-handed helical PBuTrMAM in menthol. In Figure 3, split-type CD peaks were observed at 205, 215, 225 and 245 nm, and their pattern is different from that of the highly one-handed helical poly(TrMA) that has the CD peaks at 208 and 232 nm.[22] Furthermore, the CD patterns of poly-(TrMA)[22] and poly(1-phenyldibenzosuberyl methacrylate)[14] are similar to each other but those are different from the poly(N-triphenylmethylmethacrylamide).[15] Moreover, the crystal structure of TrMA[23] is different from that of TrMAM.[24] Thus, we believe that the propeller structures of the trityl groups in the bulky polymethacrylates are likely different from that of the bulky polymethacrylamides. The CD intensity around 205 nm and optical rotation of the helical PBuTrMAMs were lower than those of the one-handed helical poly(TrMA)s. This indicates that the one-handedness of the PBuTrMAMs may not be high, and the propeller structure of the trityl group in PBuTrMAM may not effectively contribute to the optical activity and CD intensity.

The molecular weights of the polymers obtained in menthols were higher than that prepared in THF (Table II), probably because of the lower chain transfer constant of menthols. The molecular weight of the polymer obtained at 0 °C was higher than that of 60 °C. The chain transfer may more frequently occur at 60 °C. The polymer yield became very low at −20 °C. Menthol was easily solidified at this temperature and the polymerization system become heterogeneous.

The polymerization of BuTrMAM was also carried out using different amounts of (+)-menthol in hexane (Table III). The polymer exhibited the highest CD intensity when the solvent was pure (+)-menthol (Figure 4). The CD intensities of these polymers were proportional to their optical rotation (Figure 5), and the optical activity decreased with a decrease of (+)-menthol concentration in the polymerization system.

Radical Polymerization of BuTrMAM in the Presence of Optically Active Additives

Other chiral alcohols and acid, such as (+)-neomenthol (**1**), (R)-(−)-2-octanol (**2**), (R)-(−)-2-heptanol (**3**), (S)-3-hydroxytetrahydrofurane (**4**), and (R)-(+)-tetrahydrofuran-2-carboxylic acid (**5**) (Scheme 2), were also used as the optically active additives or solvents for the polymerization of BuTrMAM to enhance the optical activity or the one-handedness of the PBuTrMAM (Table IV). However, compared with menthol, these compounds did not enhance the optical


Figure 3. CD spectra of the PBuTrMAMs in THF (Table II) at r.t.

Table III. Radical polymerization of BuTrMAM in a different concentration of (+)-menthol in hexane[a]

Run	Temp. (°C)	Menthol/Hexane (v/v)	Yield[b] (%)	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	$[\alpha]_D$[d] (deg)	$[\alpha]_{365}$[d] (deg)
1	0/UV	1/0	81	30.0	5.3	−9.7	−29.3
2	0/UV	2/1	72	3.65	3.5	−7.4	−22.3
3	0/UV	1/1	67	4.88	3.6	−7.3	−22.1
4	0/UV	1/2	65	6.20	4.7	−7.1	−21.3
5	0/UV	1/3	65	4.13	4.6	−6.9	−20.8

[a]Initiator = AIBN (0.02 M), time = 24 h, [M]$_0$ = 0.5 mol/L. [b]Methanol-insoluble part. [c]Determined by SEC in THF (PMMA standard) at 40 °C. [d]In CHCl$_3$ at r.t.
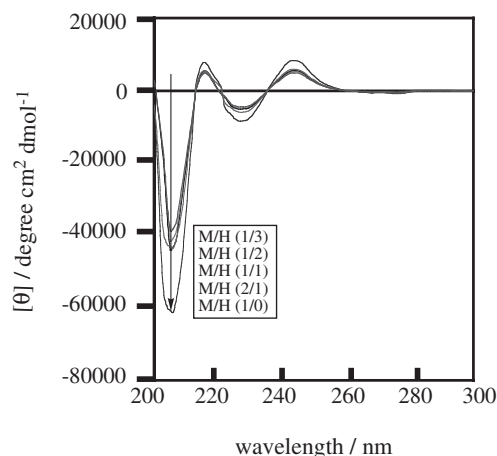
Figure 4. CD spectra of the PBuTrMAMs (polymerized in presence of different amount of (+)-menthol in hexane) in THF (Table III) at r.t.
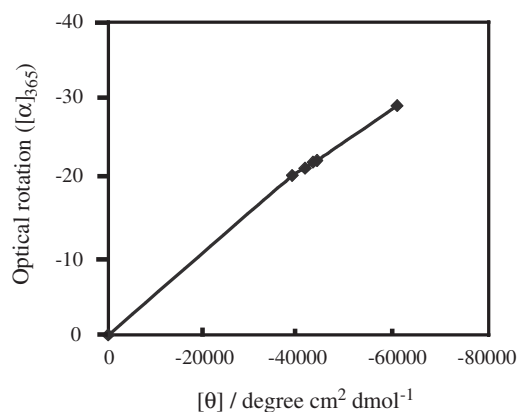

Figure 5. Plot of CD intensity at 205 nm (Figure 4) *vs* optical rotation of the PBuTrMAMs (polymerized in presence of different amount of (+)-menthol in hexane) (Table III).

activity and probably one-handedness of the polymers. When pure (+)-neomenthol (**1**) was used as the solvent (run 6, Table IV), the optical activity of the obtained polymer was higher than that of the polymer obtained in (+)-neomenthol/hexane (1/1, v/v) (run 1, Table IV). But the effect is reverse when (R)-(−)-2-octanol (**2**) was used as a solvent (run 2 and 7,
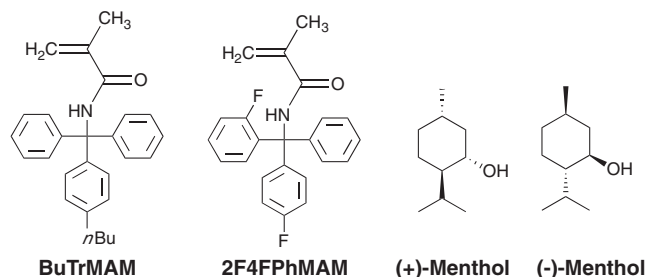

Scheme 1.
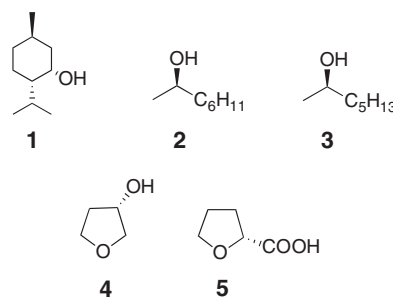
Scheme 2.

Table IV). In this case the optical activity decreased when the concentration of (R)-(−)-2-octanol increased in the polymerization solvent. The CD pattern of these polymers resembles with the polymers polymerized in presence of (+)- and (−)-menthol (Figure 6), which supports the formation of one-handed helical PBuTrMAM. The CD intensities of these polymers are low, which is probably due to the lower one-handedness of the polymers.

Chiral cobalt complexes have been successfully used for the asymmetric radical polymerization of TrMA derivatives. The radical polymerization of PDBSMA in the presence of N,N'-bis(3,5-di-*tert*-butylsalicylidene)-(1R,2R)-1,2-cyclohexanediaminatocobalt(II) (**6**) and N,N'-bis{2-(2,4,6-tri-methylbenzoyl)-3-oxobutylidene}-(1S,2S)-1,2-diphenylethylenediaminatocobalt(II) (**7**) effectively induces a single-handed helicity.[25] These Co complexes were also used as chiral additives for the polymerization of

Table IV. Radical polymerization of BuTrMAM in a mixture of chiral additive and hexane[a]

Run	Temp. (°C)	Chiral additive/Hexane (v/v)	Yield[b] (%)	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	$[\alpha]_D$[d] (deg)	$[\alpha]_{365}$[d] (deg)
1	0/UV	**1**(1/1)	79	6.3	5.84	−2.76	−9.09
2	0/UV	**2**(1/1)	91	9.1	4.58	1.8	5.4
3	0/UV	**3**(1/1)	89	6.7	4.50	1.1	3.31
4	0/UV	**4**(1/1)	90	11.8	4.68	—	—
5	0/UV	**5**(1/1)	69	1.3	3.04	0.8	2.1
6	0/UV	**1** only	76	24.7	4.45	−5.8	−16.8
7	0/UV	**2** only	89	17.9	4.33	1.01	3.1

[a]Initiator = AIBN (0.02 M), time = 24 h, $[M]_0$ = 0.5 mol/L. [b]Methanol-insoluble part. [c]Determined by SEC in THF (PMMA standard) at 40 °C. [d]In CHCl$_3$ at r.t.
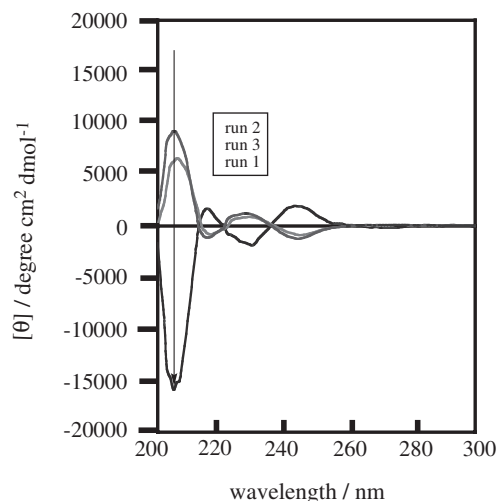
Figure 6. CD spectra of the PBuTrMAMs (polymerized in presence of different chiral additives) in THF (Table IV) at r.t.

BuTrMAM (Table V). However, the complexes functioned as the polymerization inhibitors. The optically inactive polymer was obtained in low yields only using complex **6**.

Properties of PBuTrMAMs

BuTrMAM gave highly isotactic polymers by the radical polymerization. The isotactic specificity is ascribed to the helical structure of the growing chain.[26] PBuTrMAMs have a stable helical structure. No change in CD after heating the polymer solution at $60\,^\circ$C for 10 h. The CD intensity and the pattern were also not changed while measured in different temperatures. When the polymer maintains a stable helical structure, the polymer may be separated into $(+)$- and $(-)$-fractions with opposite helicity. This was examined by the HPLC using several chiral sta-

tionary phases, but no separation has so far attained.

The optically active PBuTrMAMs obtained with $(+)$- and $(-)$-menthol at $0\,^\circ$C were coated on silica gel to be used as chiral packing materials in an HPLC column ($25\,\text{cm} \times 0.2\,\text{cm}$ (i.d.)). The chiral recognition ability of the optically active PBuTrMAM was very low. The low chiral recognition ability of PBuTrMAM might be due to the lack of the propeller structure as mentioned above and also the low one-handedness of the polymers. As mentioned before, the propeller structure of the PBuTrMAM may not clearly exist in the polymer. Since the propeller structure is chiral, the absence of this structure may result in a decrease in the chiral recognition ability of the helical chain.

The one-handed helical poly(TrMA) exhibits a high chiral recognition ability for many racemates,[27] but the polymer was easily solvolysed by the alcohols and acids used as the mobile phase in HPLC.[21] On the other hand, BuTrMAM was very stable against the solvolysis under the same conditions, and therefore, the polymer would be very valuable as a chiral stationary phase for HPLC column, if it could show a high chiral recognition.

CONCLUSIONS

The helix-sense-selective radical polymerization of *N*-(triphenylmethayl)-methacrylamide derivatives, 2F4FPhMAM and BuTrMAM, were carried out. All the polymers were nearly 100% isotactic. The free radical polymerization of 2F4FPhMAM and BuTrMAM using chiral additives gave the polymers with the optical activity and CD adsorption based on an excess right- or left-handed helical conformation. The CD intensity and the optical rotation of PBuTrMAM

Table V. Radical polymerization of BuTrMAM in the presence of optically active cobalt complex[a]

Run	Temp. ($^\circ$C)	Solvent (v/v)[e]	Cobalt complex (conc./M)	Yield[b] (%)	$M_n{}^c$ $\times 10^3$	$M_w M_n{}^c$	$[\alpha]_D{}^d$ (deg)	$[\alpha]_{365}{}^d$ (deg)
1	60	50/50 (py/ch)	**6**(0.010)	28	8.1	2.17	—	—
2	60	50/50 (py/ch)	**6**(0.020)	26	3.0	1.29	—	—
3	60	50/50 (py/ch)	**6**(0.030)	21	10.3	2.29	—	—
4	60	15/85 (py/ch)	**7**(0.020)	—[f]	—	—	—	—
5	60	50/50 (py/tol)	**7**(0.014)	—[f]	—	—	—	—
6	60	50/50 (py/ch)	**7**(0.007)	—[f]	—	—	—	—

[a]Initiator = AIBN (0.03 M), time = 24 h, $[M]_0 = 0.5$ mol/L. [b]Methanol-insoluble part. [c]Determined by SEC in THF (PMMA standard) at $40\,^\circ$C. [d]In CHCl$_3$ at r.t. [e]py = Pyridine, ch = Chloroform, tol = Toluene. [f]Not polymerized.

6

7
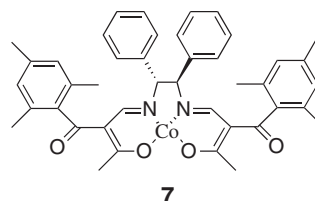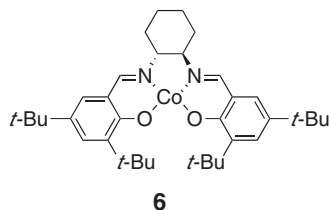
were lower than those of one-handed helical poly-(TrMA). This indicates that the one-handedness of the PBuTrMAMs may not be high. As the BuTrMAM is much stronger toward hydrolysis, the obtained polymer must be more stable when used as a chiral stationary phase for HPLC with polar alcoholic solvents. This stability would be very valuable, if one could prepare the polymer with a high chiral recognition.

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