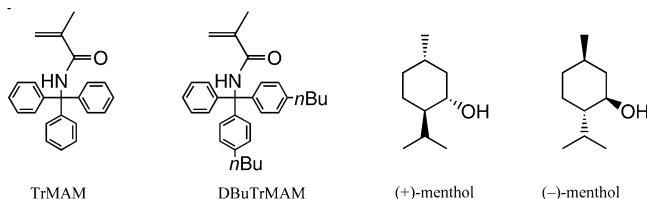# Stereospecific Radical Polymerization of *N*-Triphenylmethylmethacrylamides Leading to Highly Isotactic Helical Polymers

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Many stereoregular polymers are known to have a helical conformation in the solid state, which may be maintained even in solution if a side chain is very bulky.[1] Triarylmethyl methacrylates including triphenylmethyl methacrylate and 1-phenyldibenzosubryl methacrylate are known to produce stable one-handed helical polymers through not only an anionic process[2] but also a radical process under chiral conditions.[3] The one-handed helical polymers exhibit high chiral recognition, which enables the resolution of many enantiomers when used as chiral stationary phases for HPLC.[4] However, the ester bonds of the polymethacrylates are readily cleaved in methanol, particularly under acidic condition, which makes it difficult to study and stably use the polymers for a long time. On the other hand, amide bonds are usually stronger than the corresponding ester bonds against hydrolysis. *N*-Triphenylmethyl-methacrylamide (TrMAM) was synthesized and polymerized more than 20 years ago.[5] However, its sterical structure including stereoregularity has not yet been determined.

TrMAM DBuTrMAM (+)-menthol (−)-menthol

Recently, we found that Lewis acids, such as the rare earth triflates like Y(OTf)$_3$ and Yb(OTf)$_3$, significantly increase the isotactic specificity during the radical polymerization of the acrylamide and methacrylamide derivatives.[6−8] This prompted us to study the polymerization of bulky methacrylamides that may produce highly isotactic helical polymers. In the present study, we prepared two *N*-triphenylmethylmethacrylamides, TrMAM and *N*-[di(4-butylphenyl)phenylmethyl]methacrylamide (DBuTrMAM), and polymerized them using radical initiators under various conditions, particularly chiral conditions.

The results of the radical polymerization of TrMAM and DBuTrMAM are summarized in Table 1. In most cases, the polymers were obtained in good yields. PTrMAM was totally insoluble in common organic solvents, but PDBuTrMAM was soluble in chloroform and tetrahydrofuran (THF). Both polymers were dissolved in concentrated sulfuric acid to quantitatively produce polymethacrylamide in a short time at room temperature, which was recovered by precipitation in cold methanol. No polymer was yielded in the polymerization of TrMAM using *n*-BuLi in toluene at −78 °C.

The tacticity of the polymers was able to be estimated from the ^{1}H NMR spectrum of the derived polymethacrylamide in D$_2$SO$_4$ (Figure 1). The NMR spectrum of the polymethacrylamide prepared by the conventional radical polymerization of methacrylamide in methanol at 60 °C is also shown for comparison. The ^{1}H NMR
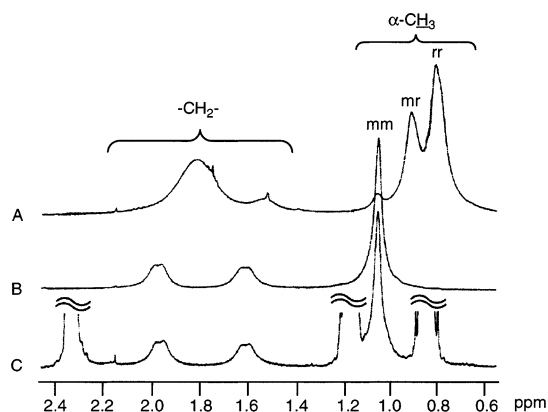
**Figure 1.** 400 MHz ^{1}H NMR spectra of PMAMs (A, obtained from radical polymerization of MAM at 60 °C in methanol; B, derived from PTrMAM (run 2 in Table 1); C, derived from PDBuTrMAM (run 8 in Table 1)) (at 60 °C in D$_2$SO$_4$). The peaks (0.85, 1.2, 2.35 ppm in spectrum C) are due to the butyl protons on the triphenylmethyl residue of the byproduct during sulfuric acid-induced decomposition.

assignment for the radically obtained polymethacrylamide has already been reported,[9] and a syndiotactic (rr)-rich polymer is formed as shown in Figure 1. On the other hand, the polymethacryl-amide obtained from PTrMAM (run no. 2 in Table 1) shows a completely different NMR pattern, and only a methyl peak due to the isotactic (mm) sequence at 1.05 ppm and two sets of doublets due to the methylene group at 1.60 and 1.95 ppm were clearly observed, indicating that the original PTrMAM is highly isotactic. When PDBuTrMAM was dissolved in D$_2$SO$_4$, an analogous spectrum pattern was observed as shown in Figure 1C. These results indicate that the radically obtained poly(*N*-triphenylmethylmeth-acrylamide)s are nearly 100% isotactic.

The PDBuTrMAMs prepared in (+)- and (−)-menthol were optically active, and their optical rotation was opposite to that of menthol. This suggests that the optical rotation is not due to the incorporation of menthol residue in the polymer. The polymer obtained at 0 °C showed the highest optical activity. The melting point of (−)-menthol is 43 °C, but all of the polymerization solution was homogeneous before polymerization was initiated. As the polymerization proceed, the solution became heterogeneous except for run 8 in Table 1. The circular dichroism (CD) spectra of the optically active PDBuTrMAMs are shown in Figure 2. Split-type CD peaks were observed at 230 and 245 nm, and their pattern is different from that for the highly one-handed helical poly-(triphenylmethyl methacrylate) that has peaks with the same CD sign around this area.[10] The CD intensity of PDBuTrMAM seems to be lower than that of the one-handed helical poly(triphenylmethyl methacrylate) with a specific rotation of [α]$_D$ +300°. This indicates that the one-handedness of the PDBuTrMAMs may not be high.

Table 1. Radical Polymerization of TrMAM and DBuTrMAM[a]

run	monomer	solvent	temp (°C)	yield[b] (%)	M_n^c (×10⁴)	M_w/M_n [c]	$[\alpha]_D^d$ (deg)	$[\alpha]_{365}^d$ (deg)
1	TrMAM	THF	−40	81				
2	TrMAM	THF	0	79				
3	TrMAM	THF	60	85				
4	TrMAM	toluene/(+)-menthol[e]	0	61				
5	TrMAM	toluene/(−)-menthol[e]	0	67				
6	TrMAM	toluene/(+)-menthol[e]	60	85				
7	TrMAM	toluene/(−)-menthol[e]	60	89				
8	DBuTrMAM	THF	0	64	7.4	3.7		
9	DBuTrMAM	hexane/THF/(+)-menthol[f]	20	91	20.1	12	−3.5	−13
10	DBuTrMAM	hexane/THF/(−)-menthol[f]	20	90	13.0	14	+3.2	+11
11	DBuTrMAM	toluene/(+)-menthol[g]	0	86	44.0	22	−22	−60
12	DBuTrMAM	toluene/(−)-menthol[g]	0	90	56.0	17	+17	+59
13	DBuTrMAM	toluene/(+)-menthol[g]	20	73	13.5	6.5	−14	−37
14	DBuTrMAM	toluene/(−)-menthol[g]	20	75	14.7	8.5	+11	+33
15	DBuTrMAM	toluene/(+)-menthol[g]	40	69	19.3	4.4	−11	−30
16	DBuTrMAM	toluene/(−)-menthol[g]	40	73	16.5	2.9	+12	+32

[a] [Monomer]₀ = 0.5 mol/L; [initiator]₀ = 0.02 mol/L; initiator, n-Bu₃B/air (run 1), AIBN (runs 2−16, UV irradiation at 0 and 20 °C); time, 24 h. [b] MeOH-insoluble part (runs 1−7); hexane-insoluble part (runs 8−16). [c] Determined by SEC in THF at 40 °C (polystyrene standard). [d] In THF at room temperature. [e] Toluene/menthol = 2/5 (v/v). [f] Hexane/THF/menthol = 1/2/12 (v/v/v). [g] Toluene/menthol = 1/100 (v/v).
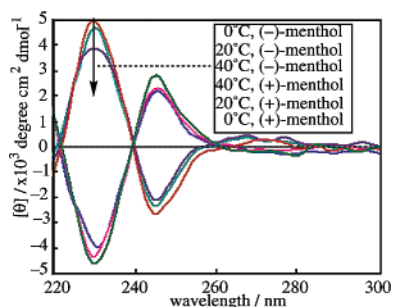
Figure 2. CD spectra of PDBuTrMAMs (runs 11−16 in Table 1) in THF at room temperature.
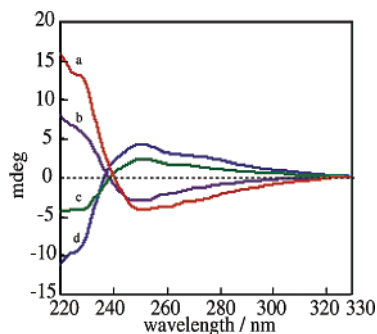
Figure 3. CD spectra of PTrMAMs (runs 4−7 in Table 1) in Nujol at room temperature (a, run 5; b, run 7; c, run 6; d, run 4).

Because PTrMAMs are insoluble in solvents, the CD spectra in solution cannot be measured, but the spectra were obtained for the polymer randomly dispersed in Nujol (Figure 3).[11] The spectral pattern is similar to that of the PDBuTrMAM obtained in the same menthol, and the CD intensity was also high for the polymer prepared at 0 °C. These results support the formation of the prevailing one-handed helical PTrMAM in menthol.[12]

TrMAM was not solvolyzed at all in methanol−chloroform (1:1) at 35 °C even after 1 week, whereas the half-life of triphenyl-methyl methacrylate under the same conditions is only 15 min.[13]

This indicates that TrMAM is much stronger toward hydrolysis and the obtained polymer must be more stable when used as a chiral stationary phase for HPLC with polar alcoholic solvents. This stability must be very valuable for the introduction of various functional groups on the phenyl groups. The soluble polymers seem to be interesting polymer samples that can be used to study the solution properties of the polymers.

Supporting Information Available: Experimental details for the monomer synthesis, polymerization, and characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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