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Synthesis of Optically Active Poly(methyl methacrylate) by Cyclopolymerization of 1,4-Di-*O*-methacryloyl-L-threitol

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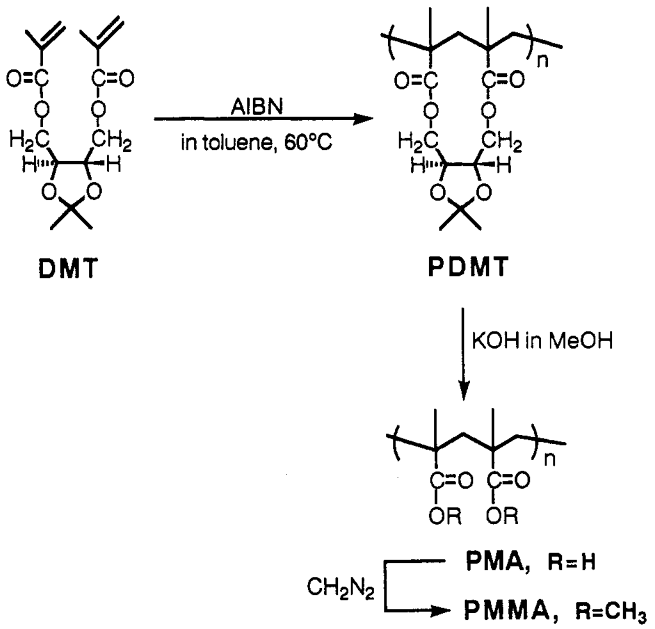
Optically active polymers due to main-chain chirality are classified according to their configurational and conformational arrangement. Polyisocyanides,[1] polychlorals,[2] and poly(triphenylmethyl methacrylate)s (PTrMA)[3] belong to the latter group. In the case of PTrMA, the bulky triphenylmethyl group is responsible for the existence of the one-handed helical polymer. Kataoka et al. reported that the radical polymerization of methacrylic acid in the presence of chitosan formed the optically active poly(methacrylic acid) (PMA) whose chirality was due to conformational asymmetry of the main chain.[4] Cram et al. reported that the polymerization of methyl methacrylate with chiral anionic catalysts yielded optically active poly(methyl methacrylate) (PMMA), but its chirality, due to a helical conformation, rapidly decreased in solution.[5] As pointed out by Okamoto et al. the bulkiness of the methyl group is insufficient for the maintenance of the stable, one-handed helical conformation of PMMA.[6] Of interest, therefore, is a possible synthetic methodology for chiral PMMA in connection with the origin of the chirality. Here we report the synthesis of optically active PMMA whose chirality is derived from the configurational stereochemistry of asymmetric carbon atoms in the main chain.

The cyclopolymerization of 2,3-*O*-isopropylidene-1,4-di-*O*-methacryloyl-L-threitol (DMT)[7] was carried out with AIBN as the initiator in toluene at 60 °C (Scheme I). After 7 h, a powdery polymer (PDMT) was obtained in 69% yield, which was soluble in benzene, chloroform, and THF, and has a number-average molecular weight (M_n) of 5.0 × 10^4. The characteristic absorption due to the methacrylic groups at δ = 5.62 and 6.16 ppm disappeared in the ^{1}H NMR spectrum as shown in Figure 1a, and hence DMT was polymerized to form the cyclic structure of 11-membered rings and the extent of cyclization was essentially 100%.

PDMT was hydrolyzed by KOH/methanol to yield PMA which was partially esterified with methanol, and then PMMA with an M_n of 2.9 × 10^4 was quantitatively obtained by the treatment of the partially esterified PMA with diazomethane. The removal of the L-threitol template from PDMT was complete, because of the disappearance of the characteristic resonance due to the template in the ^{1}H NMR spectrum of PMMA (Figure 1b). The triad tacticity was mm = 0.12, mr = 0.49, and rr = 0.39 as determined from the α-CH_3 resonance intensities. The ratio of the meso diad was larger than that for the *conventional* PMMA, which was prepared by the polymerization of MMA in toluene with AIBN at 60 °C, with mm = 0.04, mr = 0.34, and rr = 0.62. The glass transition temperature of PMMA was 108 °C, which is in agreement with the *conventional* PMMA of similar tacticity.[8]

PMMA and PMA exhibit optical activity, with a specific rotatory power ($[\alpha]^{20}_{405}$, c = 1.0 g·dL) of −4.3° in chloroform and −2.7° in methanol, respectively. The sign of these powers is opposite to that for PDMT with +98.2° in chloroform ($[\alpha]^{20}_{405}$, c = 1.0 g·dL). The CD spectrum of PDMT shows a negative Cotton effect with a minimum at 220 nm, whereas that of PMMA has a first positive and a second negative Cotton effect at 229 and 216 nm, respectively[9] (Figure 2). There is a substantial difference

Scheme I



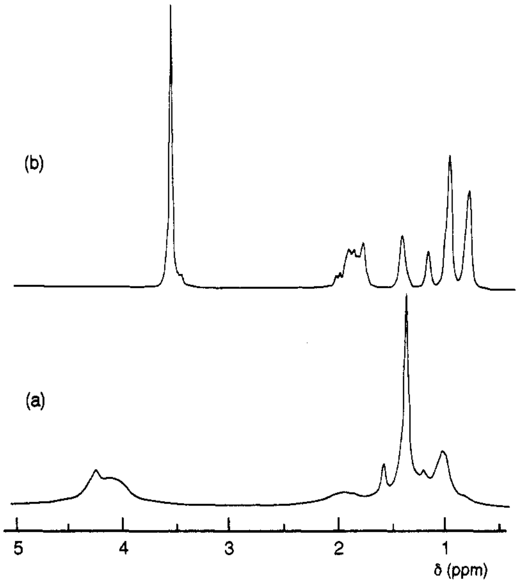


Figure 1. 400-MHz ^{1}H NMR spectra of PDMT obtained by cyclopolymerization of DMT (a) and the PMMA derived from PDMT (b). Spectra were run at 21 °C in 5% (w/w) solution in $CDCl_3$.

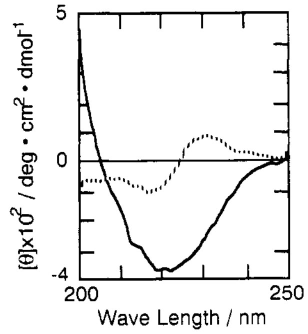


Figure 2. CD spectra of PDMT obtained by cyclopolymerization of DMT (a) and the PMMA derived from PDMT (b). Spectra were run at 25 °C in hexafluoroisopropyl alcohol.

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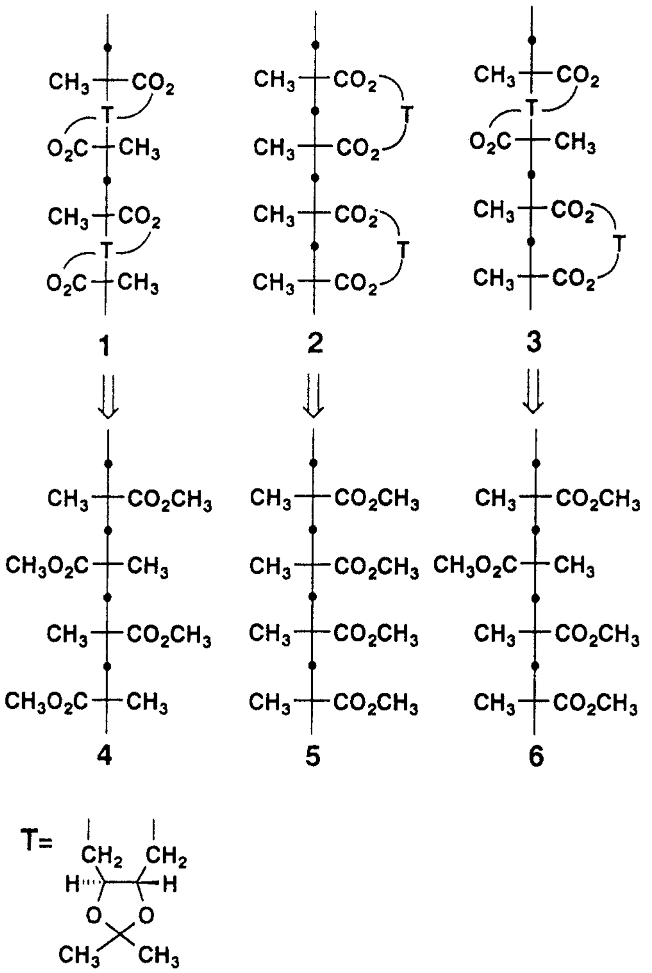
Scheme II



in chiroptical properties between these polymers. The optical activity of PMMA does not change after storage in a solution of THF for a month.

Poly(methacrylic acid-*co*-styrene)s, prepared by radical copolymerization of DMT with styrene followed by removal of L-threitol units from the resulting copolymers, exhibited optical activity.[7] The L-threitol template transmitted its chirality to the main chain in the intramolecular cyclization of DMT to form an enantiomeric, racemo cyclic unit. During the homopolymerization of DMT, the same cyclic unit must also form. The diads **1–3**, shown as Fischer projections in Scheme II, describe possible models of the polymer chain (only one enantiomer of racemo units is presented). After the removal of the template units, the racemo and meso diads **1** and **2** convert to the syndiotactic and isotactic chains **4** and **5**, respectively, which possess mirror planes and are, therefore, achiral. However, there are no symmetry elements in the heterotactic chain **6** derived from the racemo–meso diad **3**, and hence **6** is dissymmetric. In fact, a microstructure with an increased mr triad content is observed for the PMMA derived from the PDMT. In addition, the stability of the optical activity in solution shows that the chirality is due to configurational rather than helical main-chain asymmetry, involving an asymmetric carbon atom. Further studies are underway to investigate the effect of polymerization conditions on the optical rotatory power of the resulting polymers and to assign the absolute configuration of the polymer.

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(9) CD spectral measurements were carried out at 25 °C in hexafluoroisopropyl alcohol with a sample of 0.7 mg·mL. The path length of the cell was 0.1 cm.