

Stereospecific Radical Polymerization of 1-Phenyldibenzosuberyl Methacrylate Affording a Highly Isotactic Polymer

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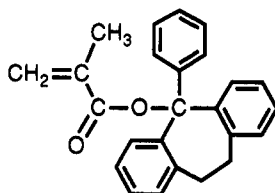
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Stereoregulation in the polymerization of vinyl monomers is one of the most important topics in polymer chemistry. Despite the fact that numerous studies have reported on highly stereoregular polymerization based on anionic and coordination mechanisms, only a few are directly concerned with radical polymerization.¹ Radical polymerization in solution usually allows for atactic polymers rich in syndiotacticity,² and isotactic polymers have only been obtained in a limited number of cases, primarily for solid-state polymerizations.³ Examples of isotactic-specific radical polymerization in solution are known to exist only for certain bulky methacrylates, such as triphenylmethyl methacrylate⁴ and diphenyl-2- and -4-pyridylmethyl methacrylates,⁵ giving rise to polymers having a triad isotacticity of mm 64%, 84%, and 76%, respectively. The isotactic specificity in these cases has been explained in terms of a steric repulsion between an ester group of an entering monomer and that of the growing chain end which prevents syndiotactic addition, and a rigid helical conformation of the growing polymer chain maintained by the bulky side groups, which enhances the isotactic addition of an entering monomer. However, the isotacticity of the obtained polymers is much lower than that of the polymers obtained by anionic polymerization. The three above-mentioned bulky methacrylates provide optically active polymers with a stable one-handed helical conformation and an almost perfect isotactic main-chain configuration through anionic polymerization with optically active initiators.⁵⁻⁷

In the present paper, stereospecific radical polymerization of 1-phenyldibenzosuberyl methacrylate (PDBSMA)⁸ is reported. This monomer gave almost perfectly isotactic polymers when polymerized with the radical initiator diisopropyl peroxydicarbonate ((*i*-PrOCOO)₂) or α,α' -azobis(isobutyronitrile) (AIBN) in toluene at temperatures between 30 and 60 °C.



PDBSMA

The polymerization results are summarized in Table I. Highly isotactic polymers with a wide range of average degree of polymerization (\overline{DP}) were obtained. Though the polymer yield was not quantitative in all cases, an ¹H NMR analysis of the hexane-soluble part of the product in polymerization at 60 °C revealed that the soluble part consisted mainly of unreacted monomer and a trace amount of oligomer, indicating that no side reaction had occurred. The isotacticity of the polymers was higher at lower temperatures (30 and 40 °C) and reached 98% in

Table I
Radical Polymerization of PDBSMA in Toluene for 24 h^a

no.	initiator	temp (°C)	yield ^b (%)	\overline{DP}^c	$\overline{M}_w/\overline{M}_n^c$	tacticity ^d mm/mr/rr
1	AIBN	60	69	179	2.34	93/4/3
2	(<i>i</i> -PrOCOO) ₂	40	86	300	2.71	98/1/1
3	(<i>i</i> -PrOCOO) ₂	30	80	490	2.61	97/2/1

^a Monomer, 0.5 g; toluene, 8 mL; [monomer]/[initiator] = 50.

^b Hexane-insoluble part (nos. 1 and 3) or methanol-insoluble part (no. 2). ^c Determined by gel permeation chromatography of poly(MMA) derived from the poly(PDBSMA) with polystyrene standards. ^d Determined on the basis of the α -methyl signals in the ¹H NMR spectrum of the poly(MMA) derived from poly(PDBSMA).

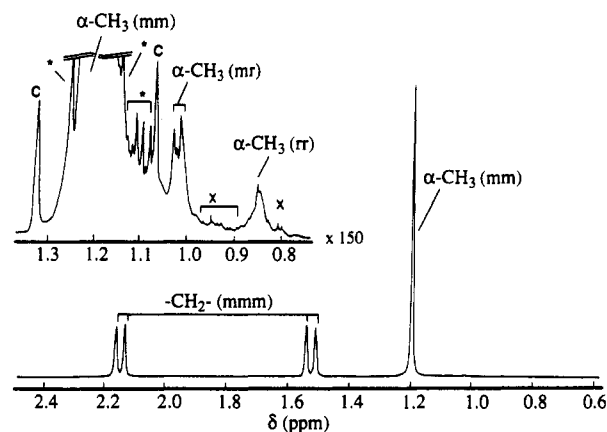


Figure 1. 500-MHz ¹H NMR spectrum of poly(MMA) derived from poly(PDBSMA) prepared at 40 °C (no. 2 in Table I) (CDCl₃, 60 °C, Me₄Si). c, *, and x denote ¹³C satellite bands, the peaks which may be due to the α -methyl group in the vicinity of the chain ends, and impurities, respectively. mmm means isotactic monomeric tetrad.¹²

polymerization at 40 °C. This degree of isotacticity is comparable to that of polymers obtained through the asymmetric anionic polymerization of bulky methacrylates at low temperatures.^{5,6a,b,d,7} It is the highest value, to our knowledge, ever reported for the radical polymerization of vinyl monomers.⁹ The difference in free energies for meso and racemo additions for polymerization at 40 °C was calculated to be ca. 2.8 kcal mol⁻¹, and for triphenylmethyl methacrylate polymerization at 60 °C (mm/mr/rr = 64/22/14⁴) ca. 0.7 kcal mol⁻¹.¹⁰ Figure 1 illustrates the ¹H NMR spectrum of the poly(methyl methacrylate) [poly(MMA)]¹¹ derived from the poly(PDBSMA) obtained at 40 °C. The spectrum has the typical pattern of an isotactic polymer.^{6d,12,13} The peaks of relatively low intensity marked by asterisks in the expanded spectrum may be due mainly to α -methyl groups in the vicinity of the chain ends.^{6d,13}

The much higher isotactic specificity in the polymerization of PDBSMA, in comparison with other bulky methacrylates, can be explained on the basis of the 1-phenyldibenzosuberyl group structure. This ester group is conformationally less flexible than triphenylmethyl and diphenyl-2- and -4-pyridylmethyl groups because the two phenyl rings are connected to each other by an ethylene group. The less flexible ester group may cause a larger steric effect between the entering monomer and the propagating chain end and may cause a more rigid helix of growing polymer chain.

The highly isotactic-specific radical polymerization of PDBSMA reported here can be applied to facilitate highly isotactic poly(methacrylic acid) and poly(MMA) sequences, through graft or block copolymerization, in other polar polymers which do not allow anionic polymerization.

Moreover, through radical polymerization including an optically active initiator or comonomer or additive, PDB-SMA may possibly afford a highly isotactic, optically active polymer with a one-handed helical conformation which so far has been prepared only by anionic or coordination polymerization of methacrylates,¹⁴ isocyanates,¹⁵ isocyanides,¹⁶ and chloral.¹⁷

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- (8) The name according to the IUPAC nomenclature system is 10,11-dihydro-5-phenyl-5H-dibenzo[a,d]cyclohepten-5-yl methacrylate. PDBSMA was synthesized from dibenzosuberone. Dibenzosuberone was converted into 1-phenyldibenzosuberol by reaction with 1-phenylmagnesium bromide, and the sodium salt of the alcohol was reacted with methacryloyl chloride to give the monomer: mp 117°C ; $^1\text{H NMR}$ (500 MHz, CDCl_3 , 35°C , Me_4Si) δ 1.98 (s, 3 H), 3.20 (s, 4 H), 5.63, 6.28 (s, 2 H), 7.08-7.42 (m, 13 H); FABMS m/z 354.1620 (calcd for $\text{C}_{25}\text{H}_{22}\text{O}_2$, 354.1618). Anal. ($\text{C}_{25}\text{H}_{22}\text{O}_2$) C, H.
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