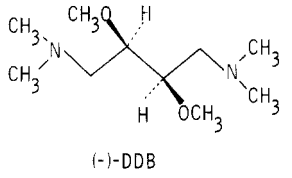
Enantiomer-Selective Polymerization of Racemic Phenyl-2-pyridyl-*o*-tolylmethyl Methacrylate Controlled by a Rigid Helix

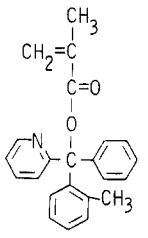
EIJI YASHIMA,[9] YOSHIO OKAMOTO,* and KOICHI HATADA

Department of Chemistry, Faculty of Engineering Science Osaka University, Toyonaka, Osaka 560, Japan.
Received September 24, 1987

Recently, we carried out the polymerization of (±)-phenyl-2-pyridyl-*o*-tolylmethyl methacrylate (PPyTMA) with (−)-2(*R*),3(*R*)-dimethoxy-1,4-bis(dimethylamino)butane [(−)-DDB]–fluorenyllithium (FlLi) complex.[1,2] The



(−)-DDB



PPyTMA

results were complicated although high enantiomeric selection was observed. We also demonstrated that in the polymerization of optically active (+)-PPyTMA by (+)- and (−)-DDB–lithium amide complexes, only (−) polymers of almost the same optical rotation were obtained.[3] It has been understood that the chiral ester group of (+)-PPyTMA forces the polymer chain to take the same helical structure regardless of the chirality of the ligand.

In the present study, in order to simplify the enantiomer-selective polymerization[4] of (±)-PPyTMA, the living poly[(+)-PPyTMA] was used for initiating the polymerization, and we could clearly demonstrated that high enantiomer selection took place only by a helical growing end.

(+)- and (−)-DDB–FlLi[5] and *N,N'*-tetramethylethylenediamine–benzyllithium (TMEDA–BzLi) complexes were used as chiral and achiral initiators, respectively. First, (+)-PPyTMA[6] was polymerized with the initiators in toluene at −78 °C to yield a living one-handed helical poly[(+)-PPyTMA]. After complete conversion of (+)-PPyTMA, racemic PPyTMA was added to the polymerization system. The results are summarized in Table I. The enantiomeric excess (ee) of unreacted monomer was determined by chiral high-performance liquid chromatography (HPLC), which completely resolved racemic PPyTMA monomer into two antipodes giving a separation factor α = 2.01. The ee of the polymer, which means the ee of the polymerized monomer, was estimated by calculation from the polymer yield and the ee of unreacted monomer.[7] The polymerization of (±)-PPyTMA initiated with (−)-DDB–FlLi showed low selectivity of the (−) enantiomer in the early stage and the ee of the polymerized monomer was only 7.2% at 13.2% polymer yield.[2] The selectivity increased as the polymerization proceeded and higher enantiomeric selection seemed to take place after the polymer grew up to a certain degree of polymerization. This was now clearly confirmed. When the living poly[(+)-PPyTMA] (DP = 30)[8] prepared with (+)-DDB–FlLi was used as an initiator, complete selection of the (+) enantiomer was achieved in the early stage of the polymerization (runs 1 and 2). The ee of unreacted monomer recovered at 16.6% conversion of (±)-PPyTMA was 20%. This means that the ee of the polymerized monomer was 100%. The high enantiomeric selection must be attributed mainly to the chirality of the growing-chain anion with rigid one-handed helical conformation. The living oligomer anion (DP = 1–5) of (+)-PPyTMA prepared with (+)-DDB–FlLi showed lower selectivity to the (+) isomer because the oligomer chains were not long enough to take a rigid one-handed helical conformation (run 4). The enantiomeric selectivity of the oligomer anions was quite similar to that of the polymerization of (±)-PPyTMA initiated by (−)-DDB–FlLi.[2] In the later stage of the polymerization, (−)-PPyTMA was incorporated into the polymer chain because of its higher concentration over (+)-PPyTMA. This brought about the steep decrease of enantiomeric selection (run 3). For high enantiomeric selection, rather long sequence of the same (+)- or (−)-PPyTMA seems necessary. The living poly[(+)-PPyTMA] (DP = 40) initiated by (−)-DDB–FlLi also polymerized the (+) isomer preferentially in spite of the use of (−)-DDB (runs 5 and 6), indicating that the enantiomeric selectivity is governed more strongly by the helical structure of poly[(+)-PPyTMA] than the chiral ligand. On the other hand, the oligo[(+)-PPyTMA] anion (DP = 1–5) initiated with (−)-DDB–FlLi polymerized the (−) isomer over the (+) isomer with low selectivity (run 7), as in the case of the polymerization of (±)-PPyTMA initiated with (−)-DDB–FlLi. These results indicate that the enantiomeric

Table I
Enantiomer-Selective Polymerization of (±)-PPyTMA by Living Poly[(+)-PPyTMA] in Toluene at −78 °C[a]

poly[(+)-PPyTMA][b]			time,	total	convrsn of		THF-sol polym				
run	initiator	DP	h	yield, %	(±)-PPyTMA	DP[c]	yield, %	$[\alpha]^{25}_{D}$,[d] deg	THF-insol polym yield, %	% ee of polym[e]	% ee[f] of unreacted monomer (α)[g]
1	(+)-DDB–FlLi	30	5.0	56.7	12.8	38	40.1	−330[h]	16.6	100	14.7 (−)
2		30	5.0	58.5	16.6	39	39.2	−317[i]	19.0	100	20.0 (−)
3		30	16.0	79.5	59.2	48	46.7	−314	32.8	42.8	62.3 (−)
4		1–5	1.5	35.5	30.1		35.5	−329[j]	0	37.8	16.3 (−)
5	(−)-DDB–FlLi	40	6.0	62.0	22.0	54	2.0	−92	60.0	43.1	12.2 (−)
6		40	15.0	76.0	51.1	59	2.5	−146	73.5	27.3	28.5 (−)
7		1–5	1.0	28.9	20.0		28.9	+8	0	14.0	3.6 (+)
8	TMEDA–BzLi	40	8.5	62.7	24.9		0		62.7	40.0	13.3 (−)
9		40	26	80.9	9.5	77	0		80.9	31.7	46.6 (−)

[a] Monomer/solvent = 1/20 (g/mL), [(±)-PPyTMA]/[Li] = 40 (mol/mol). [b] (+)-PPyTMA was completely polymerized with initiators to prepare living poly[(+)-PPyTMA]. Degree of polymerization (DP) of poly[(+)-PPyTMA] was estimated from gel permeation chromatogram of the PMMA derived from a part of the poly[(+)-PPyTMA]. [c] DP of the polymer estimated in the same manner as the poly[(+)-PPyTMA]. [d] In $CHCl_3$/2,2,2-trifluoroethanol (90/10). [e] Enantiomeric excess of the polymerized monomer calculated from the ee of unreacted monomer and conversion of (±)-PPyTMA. [f] Determined by chiral HPLC.[6] [g] Sign of optical rotation of unreacted PPyTMA. The specific rotations ($[\alpha]^{25}_{365}$) of unreacted PPyTMA (no. 1 and 2) were −48° and −65°, respectively. [h] α = −0.466° (*c* 0.282 g/dL, 0.5 dm). [i] In THF, α = −0.603 (*c* 0.380 g/dL, 0.5 dm). [j] In $CHCl_3$ at 577 nm.

0024-9297/88/2221-0854$01.50/0

selection by the rigid polymer anion is more potent than by other factors.

A more conclusive result was obtained when an achiral initiator, TMEDA–BzLi complex, was used for the preparation of living poly[(+)-PPyTMA]. Enantiomer selection was also achieved by the living anion (runs 8 and 9). In this case, the enantiomeric selection must be due to the chirality of the one-handed helix of poly[(+)-PPyTMA]. The enantiomer selectivity was much higher than that observed in the polymerization of (±)-PPyTMA by (+)-DDB–FlLi.

The work reported here may be the most clear example of chiral recognition by a growing end with a rigid one-handed helical conformation.

Registry No. (+)-PPyTMA (homopolymer), 110068-10-5; (+)-DDB, 26549-21-3; (−)-DDB, 26549-22-4; TMEDA–BzLi (complex), 15976-11-1; (±)-PPyTMA (homopolymer), 112655-43-3; FlLi, 881-04-9.

References and Notes

(1) (−)-DDB–FlLi complex gave almost optically pure one-handed helical poly(triphenylmethyl methacrylate) quantitatively, whose $[\alpha]^{25}_{D}$(THF) was −312°.
(2) Yashima, E.; Okamoto, Y.; Hatada, K. *Polym. J.* **1987**, *19*, 897–904.
(3) Okamoto, Y.; Yashima, E.; Hatada, K. *J. Polym. Sci., Polym. Lett. Ed.* **1987**, *25*, 297–301.
(4) This type of polymerization has been called asymmetric-selective or stereoelective polymerization.
(5) (+)- and (−)-DDB were dried over CaH_2 and distilled under reduced pressure. Each of them was mixed with FlLi prepared with fluorene and 1 equiv butyllithium in molar ratio [DDB]/[FlLi] = 1.2 in toluene at room temperature.
(6) (+)-PPyTMA (ee = 99.5%, $[\alpha]^{25}_{D}$ +88.6° in benzene, c = 0.94 g/dL) was obtained by optical resolution of racemic PPyTMA on a preparative chiral HPLC column packed with cellulose tris[(3,5-dichlorophenyl)carbamate] (Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Chromatogr.* **1986**, *363*, 173–186). HPLC was accomplished on a JASCO TRIROTAR-II equipped with UV (JASCO UVIDEC-100-III) and polarimetric (JASCO DIP 181C) detectors by using hexane–2-propanol (95/5 (v/v)) as eluent at 25 °C.
(7) Okamoto, Y.; Gamaike, H.; Yuki, H. *Makromol. Chem.* **1981**, *182*, 2737–2746.
(8) DP was estimated by GPC analysis of poly(methyl methacrylate) derived from poly(PPyTMA).[3]
(9) Current address: Department of Applied Chemistry, Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890, Japan.

Communications to the Editor

Thermal Stability of Benzoyl Peroxide Initiated Polystyrene

"Weak links" are known to play an important role in the initiation of the thermal degradation of polystyrene. It is also known that the initial rate of degradation is a function of the initiation mechanism (anionic versus radical)[1-5] and, for radical-initiated polystyrene, the particular initiator.[6-8] In recent publications we have reported on the nature of the initiator-derived end groups in polystyrene prepared with benzoyl peroxide as the initiator and speculated on the possible role of these end groups in the thermal and photochemical degradation of that polymer.[9,10] The various mechanisms whereby benzoyloxy groups may be incorporated into polystyrene are summarized in Figure 1.

In the course of the above-mentioned studies we prepared polystyrene with ^{13}C-labeled end groups by conducting polymerizations with benzoyl-*carbonyl*-^{13}C peroxide as the initiator.[10] This permits the various benzoyloxy ends to be readily quantified in polymers of molecular weights ≤200 000 by ^{13}C NMR. We now wish to report that we have used these polymers to assess the thermal stability of the benzoyloxy end groups present in benzoyl peroxide initiated polystyrene and to ascertain whether they constitute "weak links" in polystyrene.

The polystyrene used in this study was prepared in bulk with 0.1 M benzoyl-*carbonyl*-^{13}C peroxide as initiator and was polymerized to 80% conversion of styrene (sample E from the previous work[10]). The proportions of the various benzoyloxy end groups were determined by ^{13}C NMR—see Figure 2. Degradations were carried out in a stream of dry nitrogen in a tube furnace heated at 300 ± 10 °C. The samples (100 mg) were thinly spread on a quartz boat. Following degradation for the stated time the samples were allowed to cool while under nitrogen, weighed, then dissolved in $CDCl_3$ and the ^{13}C NMR spectra obtained. The molecular weight and molecular weight distribution of the samples were evaluated by GPC.

Examination of the NMR spectra (Figure 2) of the degraded polymers showed that after only 10 min all resonances due to secondary benzoate end groups have disappeared while the primary benzoate resonances appear essentially unchanged both in appearance and relative intensity (see below). During this time there was ≤5% weight loss and only slight broadening of the molecular weight distribution to lower molecular weights. Thus the end groups formed by head addition to monomer, transfer to initiator, or primary radical termination are thermally much less stable than those formed from normal tail addition to monomer (cf. Figure 1). This order of stability is as expected from the relative thermal stabilities of model compounds.[11]

The loss of end groups on thermolysis is likely to involve elimination to form an unsaturated end group by the normal ester pyrolysis mechanism.[11] Unsaturated ends have long been thought to be "weak links" in polystyrene.[2,4,12] Thus the secondary benzoate ends may be "weak links". It should be noted that the unsaturated ends generated from the groups formed by tail addition, head addition, and transfer to initiator or primary radical termination have different structures (see Figure 1) and may differ with respect to their ability to initiate further degradation. This and the possibility that degradation may be catalyzed by the benzoic acid byproduct released on pyrolysis warrant further investigation.

The primary benzoate ends appear to be at least as stable as, if not more stable than, the polymer backbone.

0024-9297/88/2221-0855$01.50/0