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]

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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.

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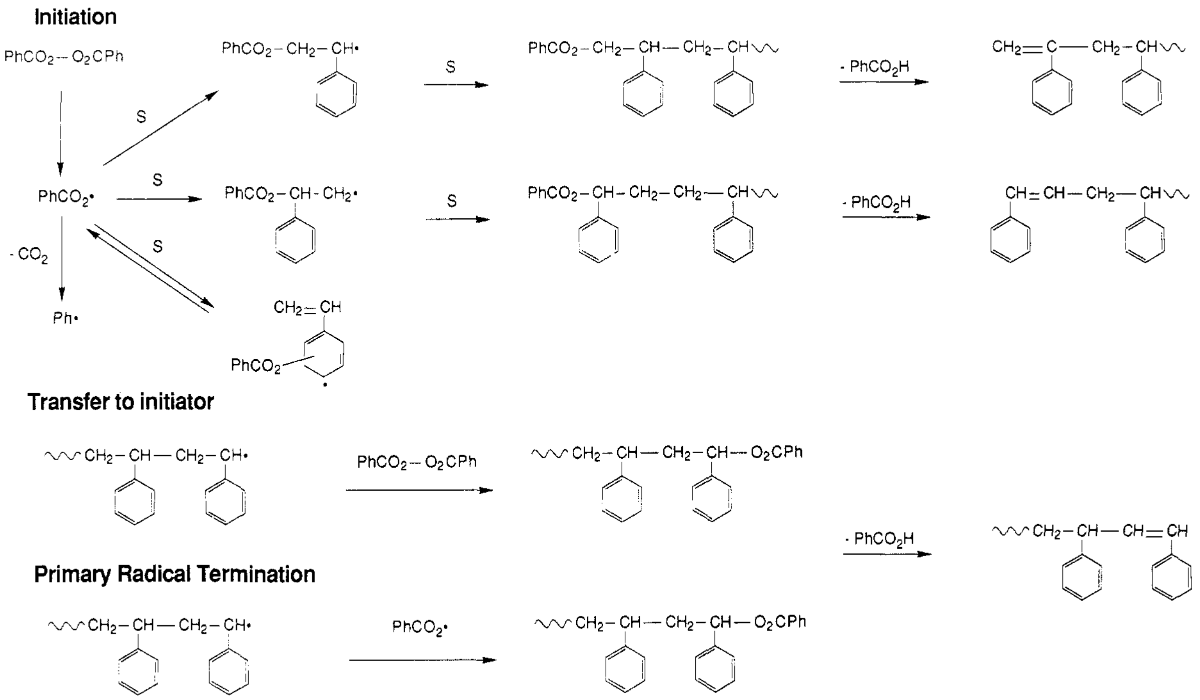

Figure 1. Mechanisms for formation of benzoate end groups during benzoyl peroxide initiated styrene polymerization[9,10] and structures of the unsaturated ends which would be formed on elimination of benzoic acid.

After 10 min the number of such end groups per styrene unit has, if anything, increased slightly (ca. 3%, an amount consistent with the slight weight loss). Even after 50% weight loss primary benzoate ends still remain. The latter end groups are clearly not "weak links" in polystyrene. Hence we can now rationalize the finding of McWalter[8] who used IR spectroscopy to show that in a (presumably) low conversion polymer the benzoate ends are just as stable as the polymer backbone.

The importance of transfer to initiator and primary radical termination is very much dependent on the polymerization conditions (initiator concentration, degree of conversion, polymerization temperature).[10] Therefore, the fraction of "weak links" in polystyrene prepared with benzoyl peroxide initiator will depend on the conditions used for its preparation. Note, however, that all benzoyl peroxide initiated polystyrenes will have a small fraction of secondary benzoate groups which are formed in initiation by head addition of the benzoyloxy radical to the monomer (see Figure 1).

The above-mentioned factors must be borne in mind when interpreting data on thermal degradation of polystyrene. Polymers prepared for studies on thermal degradation are usually prepared to low conversion.[5,8,13,14] In industry polymers are prepared under conditions which maximize conversion. Thus, the finding that the importance of both transfer to initiator and primary radical termination increases dramatically with conversion[10,15] may account for some difference of opinion as to whether polystyrene prepared with benzoyl peroxide has initiator-derived "weak links".[5,8,13] A further implication is that benzoyl peroxide initiated polystyrene should not be used when assessing the importance or otherwise of unsaturated end groups as "weak links" during thermal degradation.[14]

Studies on the thermal and photochemical stabilities of polymers prepared with appropriately labeled initiators offer a means of assessing the role of the initiator-derived functionality as "weak links" in polymer degradation. A more quantitative study of the degradation of benzoyl peroxide initiated and other polystyrenes where the disappearance of end groups will be related to changes in the molecular weight distribution is in progress.

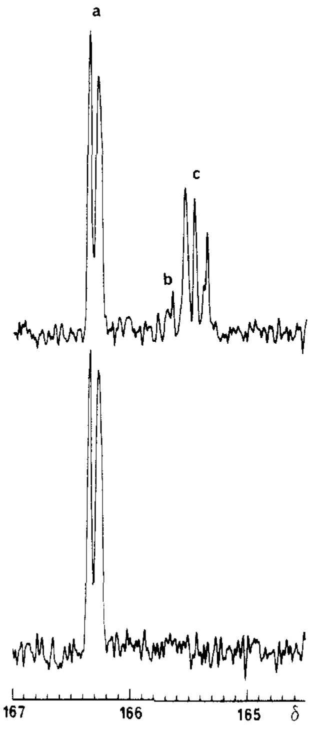

Figure 2. Carbonyl region (δ 164.5–167.0) of the 62.9-MHz ($CDCl_3$) ^{13}C NMR spectra of polystyrene samples (A) prepared with 0.1 M benzoyl peroxide to 80% conversion of styrene and (B) same as (A) but sample degraded under N_2 at 300 ± 10 °C for 10 min (see text). Peak assignments: (a) primary benzoates formed by tail addition; (b) secondary benzoates formed by head addition; (c) secondary benzoates formed by transfer to initiator or primary radical termination. In sample A the proportions of these end groups are a:b:c = 57:3:38.[10]

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Macromolecules **1988,** *21,* 857-858

Registry No. Benzoyl peroxide, 94-36-0; polystyrene, 9003-53-6.

References and Notes

(1) Guaita, M. *Br. Polym. J.* **1986,** *18,* 226-230.
(2) Lehrle, R. S.; Peakman, R. E.; Robb, J. C. *Eur. Polym. J.* **1982,** *18,* 517-529.
(3) Rudin, A.; Samanta, M. C.; Reilly, P. M. *J. Appl. Polym. Sci.* **1979,** *24,* 171-185.
(4) Cameron, G. G.; Meyer, J. M.; McWalter, I. T. *Macromolecules* **1978,** *11,* 696-700.
(5) Wall, L. A.; Straus, S.; Florin, R. E.; Fetters, L. J. *J. Res. Natl. Bur. Stand.* **1973,** *77A,* 157-170.
(6) Singh, M.; Nandi, U. S. *J. Polym. Sci., Polym. Lett. Ed.* **1978,** *17,* 121-124.
(7) Cascaval, C. N.; Straus, S.; Brown, D. W.; Florin, R. E. *J. Polym. Sci., Polym. Symp.* **1976,** *57,* 81-88.
(8) Cameron, G. G.; Bryce, W. A. J.; McWalter, I. T. *Eur. Polym. J.* **1984,** *20,* 563-569.
(9) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982,** *15,* 909-914.
(10) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982,** *15,* 1188-1191.
(11) Taylor, R.; Smith, G.; Wetzel, W. H. *J. Am. Chem. Soc.* **1962,** *84,* 4817-4824. See footnote 40 in ref 9.
(12) Costa, L.; Camino, G.; Guyot, A.; Bert, M.; Chiotis, A. *Polym. Degrad. Stab.* **1982,** *4,* 245-260.
(13) Grassie, N.; Kerr, W. W. *Trans. Faraday Soc.* **1959,** *55,* 1050-1055.
(14) McNeill, I. C.; Makhdumi, T. M. *Eur. Polym. J.* **1967,** *3,* 637-643.
(15) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1984,** *17,* 1094-1099.

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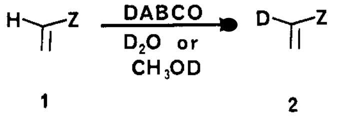
Facile Synthesis of α-Deuteriated Acrylates and Activated Vinyls

Enormous capability exists for studying reaction mechanisms and the solution and solid-state behavior of small molecules and polymers by ^{2}H NMR. In polymer characterization, for example, the molecular relaxation times available by using variable-temperature wide-line techniques spans the range of characteristic frequencies from ca. 10 MHz to 1 Hz.[1] In addition, deuteriated polymers can also be studied by neutron scattering, isotope-shifted bands in the infrared, and pyrolysis–GC–MS. New methods of deuterium incorporation at pivotal positions are vital for expanded use of these techniques.

An additional advantage in using deuteriated reactants in synthesis is that ^{2}H NMR can be used directly to follow conversion, monitor intermediate formation and disappearance, and examine side reactions and by-products. The present discovery stems from the combined use of ^{1}H, ^{2}H, and ^{13}C solution spectroscopy to monitor the synthesis of a deuteriated monomer needed for another study.[2] The specific reaction under investigation involved functionalization of acrylate esters by reaction with aldehydes in the presence of DABCO.[3] In the absence of acceptor aldehydes, and in the presence of a suitable exchangeable deuterium donor, rapid incorporation of deuterium at the α position was observed for a number of activated vinyl species ($1 \rightarrow 2$). Table I summarizes our initial results.



1 2

Z = CO$_2$R, CN, COR

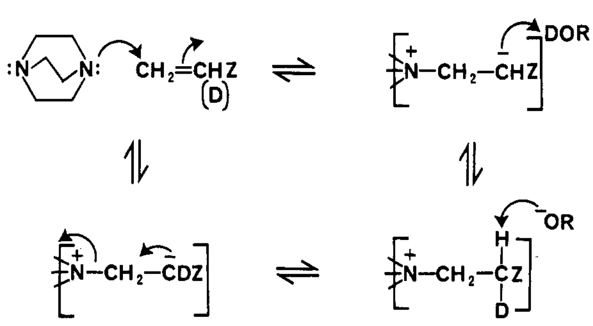


Figure 1. Proposed mechanism for α-H/D equilibration.

Table I
Summary of Reaction Conditions

compound	reactn conditions	% deuterium[a] found	% deuterium[a] theor
methyl acrylate	30 min/CH$_3$OD	93.7	91.6
butyl acrylate	30 min/CH$_3$OD	81.8	93.7
acrylonitrile	30 min/CH$_3$OD	90.5	88.2
acrylonitrile	10 min/D$_2$O	82.0	94.0
acrylonitrile	after second exchange	92.7	96.0

[a] Determined by integration of the vinyl region of the ^{1}H NMR spectra.

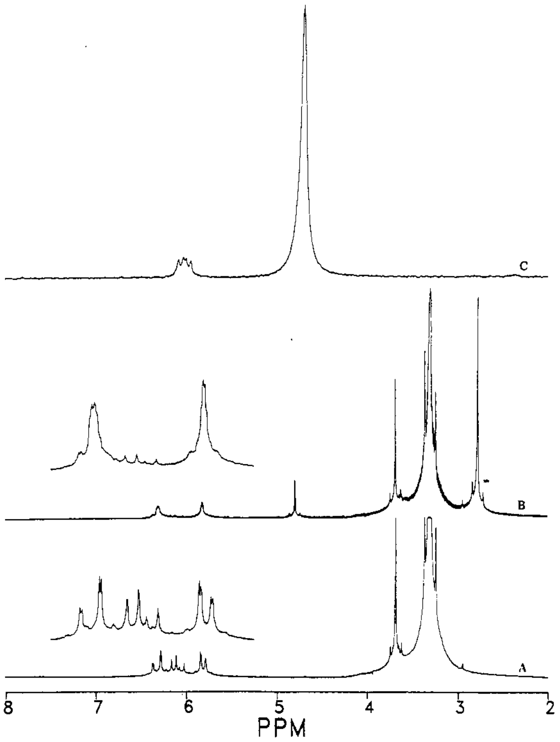


Figure 2. (A) ^{1}H spectrum of undeuteriated methyl acrylate, (B) ^{1}H spectrum of methyl acrylate-α-d, and (C) ^{1}H-coupled ^{2}H spectrum of methyl acrylate-α-d.

We propose a DABCO-catalyzed equilibration (Figure 1) in which deuterium incorporation can be driven to high levels by use of a large excess of the deuterium donor. Levels of incorporation greater than 80% were obtained in minutes with a single exchange process. This procedure is straightforward in contrast to previously reported multistep methods of α–deuteriation of acrylates.[4-6]

While either CH$_3$OD or D$_2$O served in the exchange for acrylonitrile, hydrolysis of the intermediate species formed from acrylate esters occurred in D$_2$O. In addition, higher alkyl esters underwent minor transesterification to methyl acrylate if the exchange reaction was extended. Exchange of methyl vinyl ketone was complete in a matter of min-

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