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Catalytic Chain Transfer Isomerization Reactions Involving 2-Phenylallyl Alcohol

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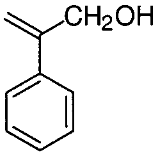
ABSTRACT: A catalytic chain transfer agent, bis[(difluoroboryl)dimethylglyoximato]cobalt(II) (COBF), was utilized in free radical polymerizations involving 2-phenylallyl alcohol (PAA). In homopolymerization only oligomers were formed, and the predominant product was 2-phenylpropanal consistent with a radical-induced isomerization reaction. In copolymerizations with methyl methacrylate (PAA included at 5 and 10 mol %) the chain transfer constants increased significantly (compared to those obtained for methyl methacrylate homopolymerization). NMR analyses of the co-oligomer chains confirmed PAA incorporation into the copolymers and provided evidence for the presence of an aldehyde group resulting from chain transfer isomerization. Further analyses by matrix-assisted laser desorption ionization (MALDI) mass spectrometry indicated conclusively that a PAA monomer unit was incorporated into copolymer chains. The thermal degradation behavior of the oligomers was measured using thermogravimetric analysis (TGA). The thermograms clearly indicate that the PAA is situated at the chain ends of the majority of the polymer chains even at low concentrations of PAA in the initial monomer feed.

Introduction

Chain transfer reactions are widely used for controlling molecular weight in free radical polymerization reactions. In some instances functional chain transfer agents have been adopted to allow the inclusion of functional end groups into the polymer chains. In the specific case of catalytic chain transfer reactions[1] with cobaloximes or porphyrins the chain transfer agent is not incorporated into the polymer chain, and therefore chain end functionalization has been restricted to vinyl end groups formed via H-abstraction from the growing radical.[2,3] In earlier work[4] it has been shown that α-methylstyrene is a particularly useful comonomer in catalytic chain transfer polymerizations as it can be used to induce high levels of reactive vinyl-terminated oligomers in many catalytic chain transfer polymerizations.

In conventional organic synthetic chemistry there is substantial interest in developing strategies for the enantioselective isomerization of allylic alcohols. Tanaka et al.[5] have recently published the use of a rhodium/phosphaferrocene complex for catalysis of such isomerizations. In synthetic polymer chemistry the generation of aldehyde end groups on oligomeric chains has appreciable potential as the aldehyde functionality is a useful group for subsequent chain extension or cross-linking.[6] In a recent communication,[7] it was shown that a novel chain transfer isomerization reaction can be induced using a catalytic chain transfer agent with the monomer ethyl α-hydroxymethyl acrylate, as shown in Scheme 1, generating an aldehyde chain-end functionality on the product oligomers. The work described in this paper extends the initial discovery by utilizing 2-phenylallyl alcohol (PAA) (IUPAC nomenclature: 2-phenylprop-2-en-1-ol) (**I**) as a monomer in catalytic chain transfer polymerizations.



(I)

The use of PAA as a functional monomer in polymerization reactions has been described in two early patents.[8,9] These patents state that PAA readily homo- and copolymerizes with a range of common vinyl monomers, such as acrylonitrile, methyl methacrylate, and methyl acrylate. However, careful scrutiny of the data contained in these patents indicates that the polymerization yields are low despite very long reaction times. In addition, PAA is claimed to act as a "moderator" in methyl methacrylate polymerization, mitigating the gel effect. Therefore, it seems that the available experimental evidence indicates that PAA does undergo polymerization, but its propagation rate is very slow and thus chain transfer (to monomer or extraneous transfer agent) may play a significant role in its polymerization kinetics. This scenario is entirely consistent with the known propagation kinetics of α-methylstyrene, in which steric hindrance induced by the α-methyl group significantly reduces the propagation rate compared to styrene.[10] In addition, there is a thermodynamic effect, resulting in a low ceiling temperature for α-methylstyrene caused by 1,3 interactions in the product polymer. The kinetics and thermodynamics of hindered monomer structures can thus be exploited for molecular weight control[11] and, in some instances, for the incorporation of chain-end functionality.

Experimental Section

Materials. The bis(methanol) complex of COBF (**II**) was prepared according to the method described by Bakac et al.[12] Methyl methacrylate (MMA; Aldrich, 99%) was passed through

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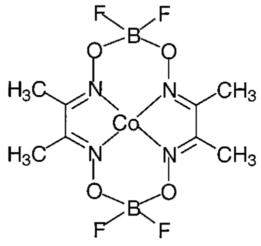
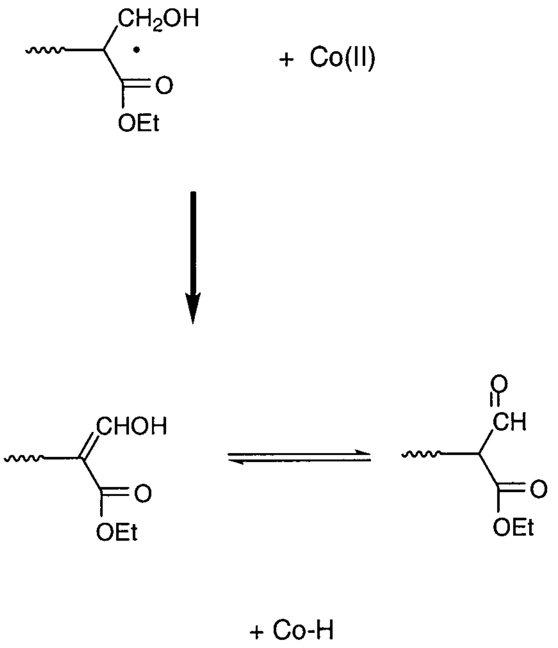
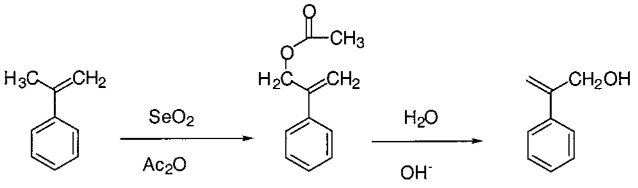


(II)

Scheme 1



Scheme 2



a column of activated basic alumina (ACROS, 50−200 μm) and purged with high-purity nitrogen (BOC) for 1.5 h prior to use. AIBN (DuPont) was recrystallized twice from methanol and used as the initiatior. PAA (**I**) was synthesized according to a procedure given by Hatch and Patton,[13] which is summarized in Scheme 2. ^{1}H NMR ($CDCl_3$): δ 1.7 (s, 1H, $-CH_2O\mathbf{H}$), 4.6 (s, 2H, $-C\mathbf{H_2}OH$), 5.4 (s, 1H, $=C\mathbf{H_2}$), 5.5 (s, 1H, $=C\mathbf{H_2}$), 7.4 (m, 5H, aromatic) ppm.

Homopolymerization of PAA in the Presence of COBF. Several reactions were run with a 50% v/v solution of PAA in toluene at 45 °C. The concentrations of AIBN and COBF used were 1×10^{-2} and 1.7×10^{-4} M, respectively. The reactions were allowed to proceed for 200 h prior to analyses.

General Copolymerization Procedure. Two stock solutions were prepared: (i) an initiator stock solution and (ii) a catalyst stock solution. (i) The initiator solution was prepared by dissolving approximately 130 mg of AIBN in 50 mL of the monomer mixture. (ii) The catalyst stock solution was prepared by dissolving approximately 2 mg of COBF into 10 mL of solution (i) and a subsequent 10-fold dilution with solution (i). Different reaction mixtures were then prepared, each containing varying ratios of the two stock solutions. Reaction ampules, specially modified for use with standard Schlenk equipment, were employed for all experiments, and care was taken to exclude oxygen at every stage. All reactions were carried out in a thermostated water bath at 60 °C. Final conversions were maintained below 3%.

Density Measurement. The density of PAA at 60 °C was determined using an Anton Paar DMA 5000 density meter and is reported as 1.016 91 g cm^{-3}.

Molecular Weight Analysis. Molecular weight distributions were determined by size exclusion chromatography using a Shimadzu LC-10 AT VP pump, a Shimadzu SIL-10AD VP autoinjector, a column set consisting of a Polymer Laboratories 5.0 μm bead-size guard column (50 × 7.5 mm) followed by three linear PL columns (10^5, 10^4, and 10^3 Å), and a Shimadzu RID-10A differential refractive index detector. Tetrahydrofuran (BDH, HPLC grade) was used as eluent at 1 mL min^{-1}. Calibration of the SEC equipment was performed with narrow poly(methyl methacrylate) standards (Polymer Laboratories, molecular weight range: $200-1.6 \times 10^6$).

Matrix-Assisted Laser Desorption Ionization (MALDI) Mass Spectrometry Analysis. MALDI analyses were either carried out on a Perseptive Biosystems, Voyager DERP instrument operated in reflectron mode or a Kratos Kompact III MALDI-TOF-MS operated in linear mode. The matrix used was 2,5-dihydroxybenzoic acid (DHB), with NaCl as the cation source. The matrix and cations were dissolved in a 50/50 methanol/water mixture. The polymers to be analyzed were dissolved in THF at a concentration of approximately 5 mg mL^{-1}. The matrix−cation solution was deposited onto the target, and the solvents were allowed to evaporate while being stirred. When completely dry, the polymer solution was placed on the dry crystals. The THF was allowed to evaporate with constant stirring.

NMR. ^{1}H NMR analyses were performed on a 300 MHz (Bruker ACF 300) spectrometer using $CDCl_3$ (Aldrich, 99.8 atom % D) as the solvent.

Thermogravimetric Analyses (TGA). Thermal degradation of the polymer products was studied under a nitrogen atmosphere using a TA instruments TGA 2050 thermogravimetric analyzer at a heating rate of 20 °C min^{-1} using sample weights in the range 5−10 mg.

Results and Discussion

Homopolymerization of PAA. The initial experiments focused on proving that the chain transfer isomerization mechanism would work in the homopolymerization of PAA. In the very early stages of the work it became clear that PAA is quite reluctant to polymerize, and only low oligomer yields could be obtained. In the presence of COBF, a straightforward radical-induced isomerization of PAA to 2-phenylpropanal was observed to occur, as shown in Figure 1, in which the ^{1}H NMR spectrum of the product clearly indicates the presence of aldehyde functionality.

Copolymerization of PAA with MMA. Copolymerization experiments were conducted at two specific feed compositions, viz. MMA with 5 and 10 mol % PAA. In previous work the criteria for efficient end group functionalization in copolymerization by CCT were set out within the framework of a kinetic model.[14] The aim of the current experimental study was to determine the extent of end group aldehyde functionality on the copolymer chains, the efficiency of the chain transfer reaction, and the total number of PAA units per oligomer chain.

Chain Transfer Reactions. The standard method for evaluating chain transfer coefficients is via the Mayo equation (eq 1):[15]

$$\frac{1}{\mathrm{DP_n}} = \frac{(1+\lambda)\langle k_t\rangle[\mathrm{R}^\bullet]}{k_p[\mathrm{M}]} + C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} \qquad (1)$$

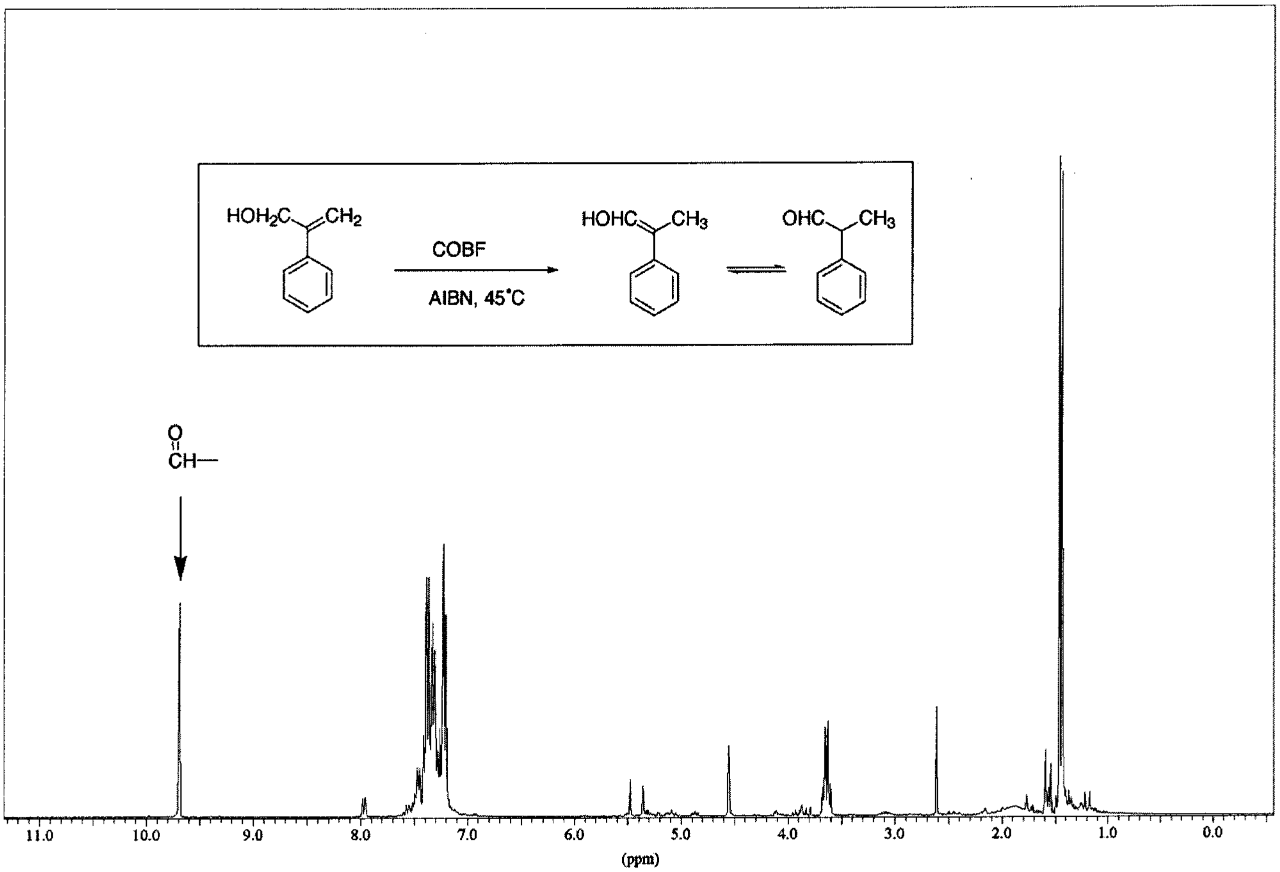


Figure 1. ^{1}H NMR spectrum showing the product, 2-phenylpropanal, obtained from the catalytic radical-induced isomerization of PAA.

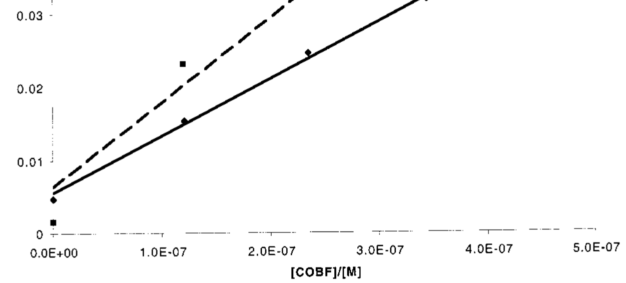


Figure 2. Mayo plots for the determination of C_s values for transfer to COBF with the feed MMA + 5 mol % and 10 mol % PAA.

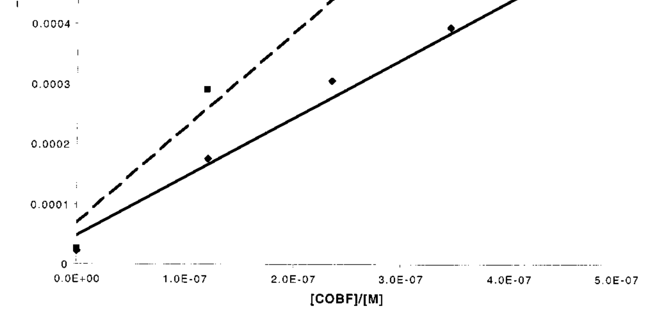


Figure 3. CLD plots based on Λ_{peak} for the determination of C_s values for transfer to COBF with the feeds MMA + 5 mol % and 10 mol % PAA.

where $\mathrm{DP_n}$ is the number-average degree of polymerization, $\langle k_t \rangle$ the average termination rate coefficient, $[\mathrm{R}^\bullet]$ the total radical concentration, k_p the propagation rate coefficient, [M] the monomer concentration, C_M the chain transfer to monomer constant, C_s the chain transfer to transfer agent constant, λ the fraction of chains undergoing disproportionation reactions, and [S] the concentration of chain transfer agent. In this work, the chain transfer constant, C_s, was taken as the slope of the resulting straight line plot, as shown in Figure 2. Addition of PAA to MMA in the CCT polymerization resulted in a substantial increase in the chain transfer constant: the C_s values obtained from the Mayo procedure are given in Table 1. The Mayo plots were generated either using the M_n values directly or by assuming $\mathrm{DP_n} = M_w/(2m_0)$ where m_0 is the mass of the monomer. Recent work on CCT has shown the latter method to be generally more reliable.[14]

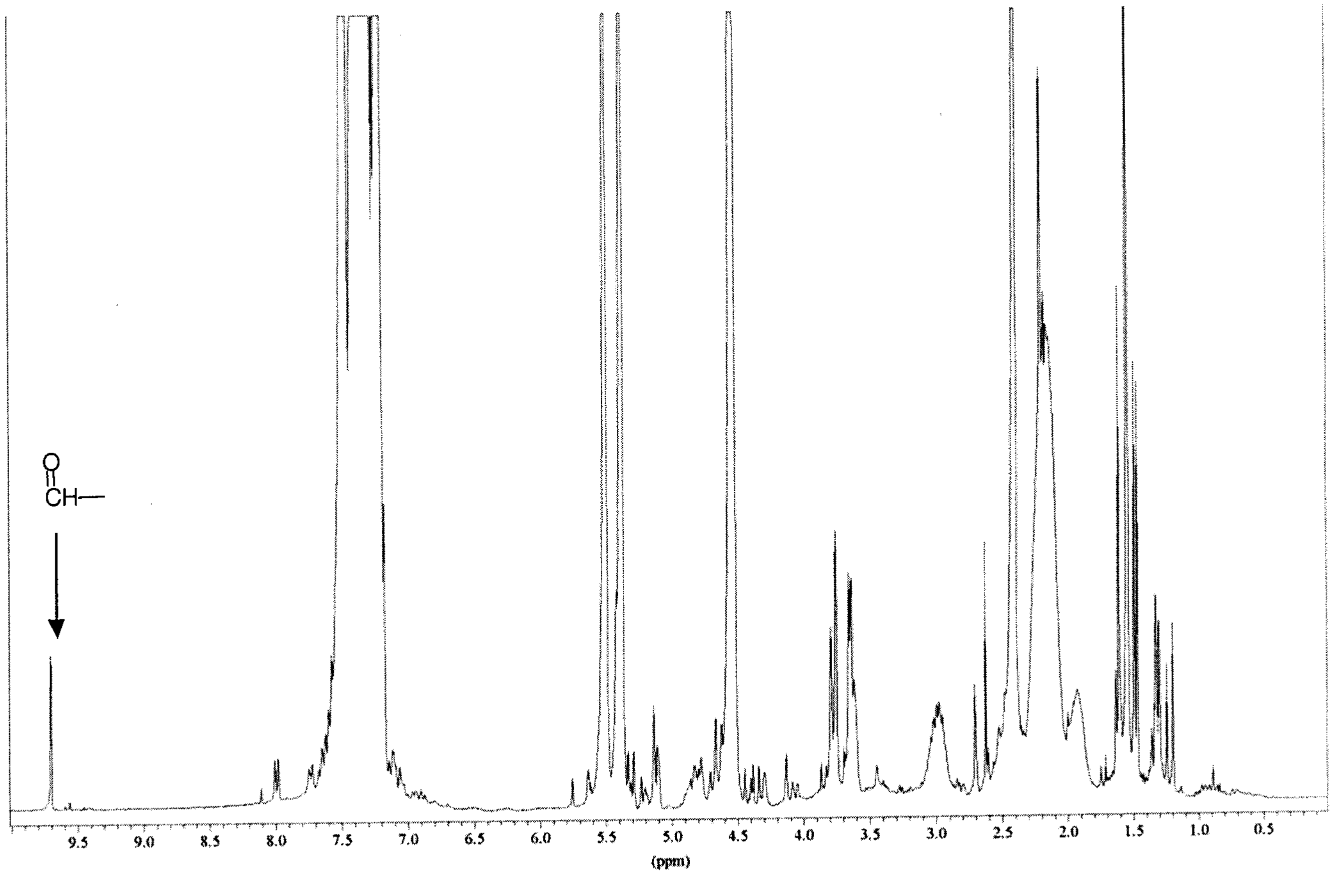


Figure 4. ^{1}H NMR spectrum of a copolymer made from a feed of MMA + 25 wt % PAA.

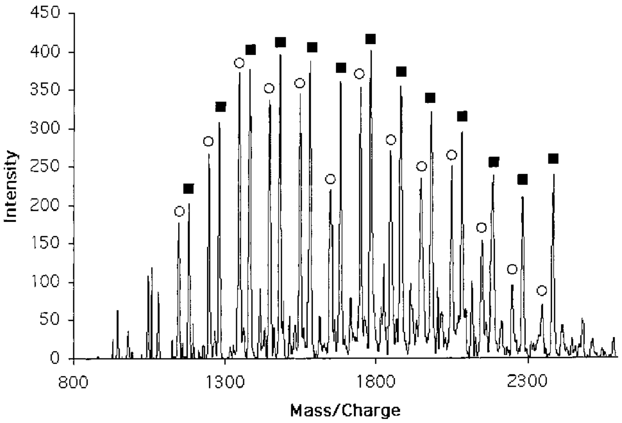


Figure 5. MALDI-MS spectrum of the copolymer obtained from the feed MMA + 5 mol % PAA. The spectrum contains two different series of peaks corresponding to chains with and without a PAA unit. The two series are denoted by either an open circle or a solid square.

Another method of determining chain transfer constants is the chain length distribution (CLD) method.[16−18] In recent work on catalytic chain transfer reactions, we have found that combining the CLD and Mayo methods can lead to complementary information. In general use, the two methods are identical and should yield the same C_s value. However, in certain cases different values are obtained. This is especially true when catalyst poisoning occurs: in this case the higher molecular weight chains tend to get formed later in the polymerization process (as there is less active catalyst), and therefore the C_s values obtained from the Mayo and CLD methods differ quite substantially (as they utilize different parts of the molecular weight distribution).[19] The CLD procedure developed by Gilbert and co-workers[16−18] is based upon taking the high molecular weight slope of the number distribution ($P(M)$) plotted as $\ln(P(M))$ vs M. The high molecular weight slope of this plot, denoted as Λ_{high}, is defined as follows:

$$\Lambda_{\mathrm{high}} = \lim_{M\to\infty} \frac{\mathrm{d}\ln(P(M))}{\mathrm{d}M} = -\left(\frac{\langle k_t\rangle[\mathrm{R}^\bullet]}{k_p[\mathrm{M}]} + C_{\mathrm{M}} + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]}\right)\frac{1}{m_0} \quad (2)$$

Measurement of C_s in this case involves the measurement of Λ_{high} as a function of [S]/[M], and a plot of $-\Lambda_{\mathrm{high}} m_0$ vs [S]/[M] then yields a straight line with slope C_s. Two groups[20,21] have recently reported that optimal results are obtained when the slope at the peak of the molecular weight distribution (Λ_{peak}) is utilized, and this is often preferable to using Λ_{high}, provided the polymerization is truly transfer dominated. The CLD plots for the different copolymerizations are shown in Figure 3. The C_s values derived from the CLD analyses are also reported in Table 1. The plots are quite linear, and there is no evidence of broadening in any of the molecular weight distributions. The agreement between the CLD and Mayo methods indicates that significant catalyst poisoning did not occur over the limited conversion range of these experiments. Quite clearly, inclusion of PAA enhances the transfer process. We speculate that the enhancement of C_s is primarily due to a retarded k_p in these copolymerizations.

Evidence for PAA Inclusion in the Oligomers and for Aldehyde End Groups. The enhanced transfer process in the presence of PAA is strong evidence

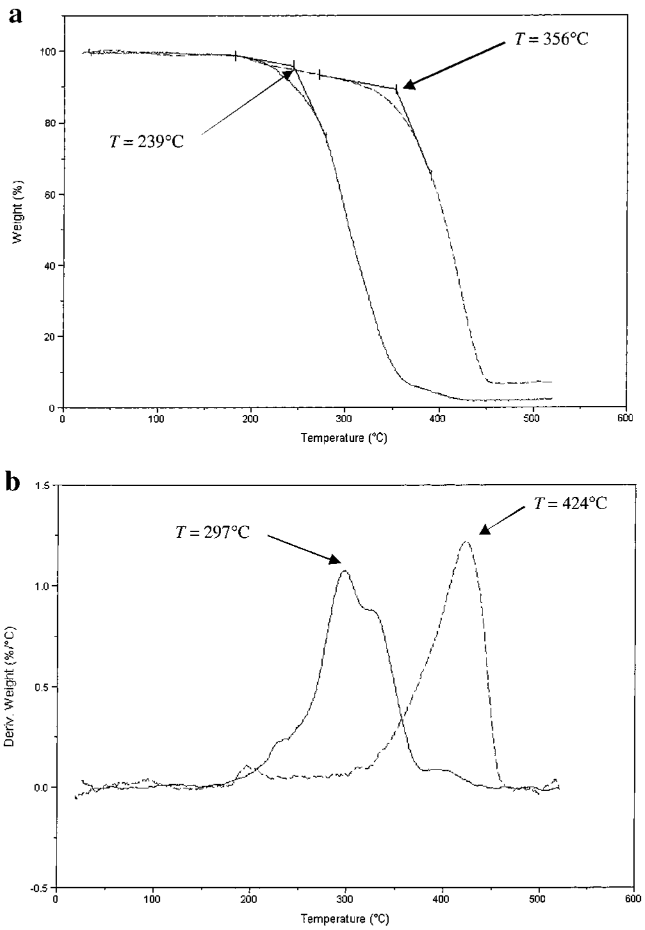


Figure 6. (a) TGA thermograms showing the onset temperatures for weight loss for samples made by catalytic chain transfer. The solid line is a PMMA polymer, and the dashed line is a 10 mol % PAA/MMA copolymer. (b) Differential TGA thermograms showing the onset temperatures for weight loss for samples made by catalytic chain transfer. The solid line is a PMMA polymer, and the dashed line is a 10 mol % PAA/MMA copolymer.

Table 1. C_s Values for Transfer to COBF for MMA and the Two Copolymer Systems with 5 and 10 mol % PAA, Utilizing the Four Different Analytical Approaches Described in the Text[a]

	Mayo		CLD	
f_{PAA}	M_n	M_w	Λ_{peak}	Λ_{high}
0	25 000	32 200	32 100	35 500
0.05	78 000	91 500	97 600	91 200
0.05	65 900	82 500	93 300	79 200
0.10	115 200	139 600	157 600	138 200
0.10	115 800	138 600	151 600	141 100

[a] The best values are generally obtained using M_w or Λ_{peak}. The copolymer transfer determinations were performed in duplicate.

for PAA inclusion. The main problem with applying NMR is the isolation of the oligomer chains from the monomer; as a consequence, we could not be sure that all monomer (especially PAA as it has a very high boiling point) was removed from the copolymers. To enhance the prospect of identifying the end group, we adopted a feed of MMA with 25 wt % PAA. As the resulting polymer samples were oligomeric, separation by precipitation was not feasible. The NMR spectrum shown in Figure 4 indicates PAA incorporation into the polymer and evidence for the isomerization reaction to the aldehyde. Confirmation that PAA was incorporated in the copolymer was obtained by the application of MALDI-MS. The MMA samples with both 5 and 10% PAA were analyzed on the Kratos Kompact III spectrometer, and the samples with 5% PAA were also analyzed on a Perseptive Biosystems, Voyager DERP instrument, which provides a more accurate mass analysis. A typical MALDI spectrum obtained on the Kratos Kompact III is shown in Figure 5, clearly showing two series of peaks corresponding to a separation of ca. 100 amu (MMA monomer unit) and 134 amu (PAA monomer unit). The strength of MALDI is that the spectra clearly show PAA incorporation. However, MALDI cannot be employed to confirm either the location of the PAA unit in the chain or the isomerization product. Careful scrutiny of the peak masses indicates that some fragmentation may be occurring in the MALDI ionization process, as noted previously for styrene-terminated polymer chains.[22,23]

TGA has been used previously to quantitatively ascertain the nature of end groups generated in catalytic chain transfer reactions.[24−27] The thermal degradation behavior of MMA oligomers produced by catalytic chain transfer in the presence and absence of PAA was measured under nitrogen. The resultant thermograms are shown in Figure 6a,b. The degradation behavior of the vinyl-terminated MMA oligomer has an onset around 240 °C and a maximum degradation rate around 300 °C. When 10% PAA was present in the feed, the thermal stability of the resultant polymer was significantly enhanced, indicating that the chemical structure of the end group had been affected. In this case the vast majority of chains experience onset degradation at 360 °C with a maximum degradation rate at 424 °C. These results provide powerful evidence that the PAA is present in the majority of the chains as an end group unit.

Conclusions

This work has shown that the novel mechanism of catalytic chain transfer isomerization is not confined to acrylic derivatives. The radically induced isomerization reaction of PAA to 2-phenylpropanal has been demonstrated. Copolymerization reactions of PAA with MMA in the presence of cobaloxime also indicate catalytic chain transfer isomerization. Evidence to support the proposed mechanism in polymerization reactions has been accumulated from a variety of experiments. Chain transfer rate constants indicate PAA has a significant impact on enhancing the chain transfer process at low levels of PAA in the feed. NMR analyses of the polymers confirm the presence of aldehyde groups and PAA incorporation. MALDI-MS also provides indisputable evidence that PAA is present in the copolymer. Finally, TGA thermograms of the polymer degradation processes provide strong supporting evidence that PAA is incorporated in the vast majority of chains as the end group unit. This novel synthetic approach provides a facile method for incorporating aldehyde chain-end functionality into oligomer chains in one step.

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