Model Copolymerization Reactions. Evidence against Concerted Complex Addition in Reactions of Simple Alkyl Radicals with *N*-Phenylmaleimide and Donor Olefins

Glenn S. Prementine[†] and Sharon A. Jones[‡]

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

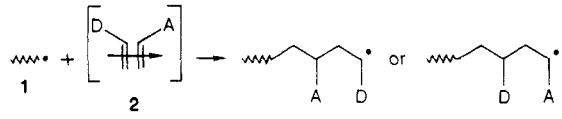
David A. Tirrell*

Department of Polymer Science & Engineering, University of Massachusetts, Amherst, Massachusetts 01003. *Received April 20, 1988*

ABSTRACT: Reductive demercuration was used to generate the 1-butyl and benzyl radicals in mixtures of *N*-phenylmaleimide (NPM) and either of the donor olefins styrene or 2-chloroethyl vinyl ether (CEVE). In each case, the major products of the reaction were derived from simple addition of the radical to NPM followed by transfer of a hydrogen atom to the initial adduct. Careful mass balances on NPM showed that mechanisms other than simple addition did not constitute important pathways for monomer consumption. These results argue against mechanistic schemes for radical copolymerization in which 1:1 monomer complexes add in a concerted manner to growing macroradicals.

Introduction

Do alkyl radicals add in a concerted manner to electron donor–acceptor (EDA) complexes formed from electron-rich and electron-poor olefins? The radical copolymerizations of such olefin pairs are anomalous in several respects, and certain of these anomalies can be explained by a polymerization scheme in which a 1:1 comonomer complex **2** undergoes concerted addition to the growing polymeric radical **1**. In particular, the "complex



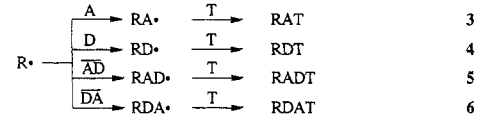
1 2

participation" model of copolymerization accounts for the formation of alternating copolymers,[1] for the facile copolymerization of monomers that homopolymerize only reluctantly, and for variations in overall copolymerization rate with changes in temperature, solvent, and monomer concentration.[2,3] Butler and co-workers have also suggested that complex participation might be required to explain the stereochemistry,[4-6] or the regiochemistry,[7] of certain radical copolymerizations. EDA complexes are observed spectroscopically in many of the reaction mixtures that afford alternating copolymers, and convincing evidence has been provided for complex participation in the *initiation* of polymerization.[8]

But this is circumstantial evidence. The concerted addition hypothesis is subject to *direct* experimental test, as shown in Scheme I: *If the radical R• adds the donor–acceptor complex $\overline{AD}$ in a single step, trapping of the simple olefin adducts RA• and RD• will not be observed.* Determination of the yields of trapping products **3** and **4** then allows an estimate of the maximum extent to which the complex participates in the consumption of monomers A and D. This work is based on the straightforward notion that concerted complex addition is unlikely to play an important role in copolymerization if it cannot be demonstrated that simple alkyl radicals undergo this reaction.

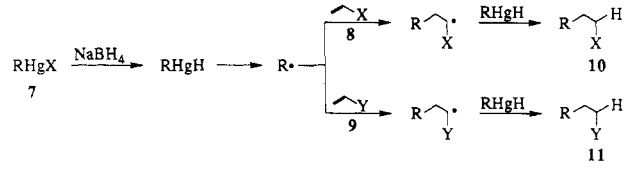
A convenient trapping method is provided by the hydride reduction of organomercurials.[9] Specifically, boro-

Scheme I



A = acceptor olefin D = donor olefin $\overline{AD}$ = complex T = trap

Scheme II



hydride reduction of alkylmercuric halides (**7**) in mixtures of olefins **8** and **9** leads to competitive olefin addition and to the formation of products **10** and **11** by efficient hydrogen atom transfer from mercury (Scheme II). With certain organomercurials, e.g., benzylmercuric chloride (vide infra), trapping by transfer of an alkyl fragment is also observed. The intermediacy of free radicals in reductive demercuration has been established most convincingly by the use of the 5-hexenyl radical cyclization,[10] by correlation of product distributions from demercuration and tin hydride reduction,[11] and by trapping of reaction intermediates by 2,2,6,6-tetramethylpiperidoxyl or by molecular oxygen.[12,13] Particularly germane to the present work is Giese's observation that radical reactivities determined by the "mercury method" can be correlated with reactivity parameters derived from radical copolymerizations.[14,15]

We describe in this paper the use of the mercury method to determine the extent to which concerted complex addition competes with conventional olefin addition when simple alkyl radicals (1-butyl and benzyl) are generated in mixtures of *N*-phenylmaleimide (NPM) and the donor olefins styrene or 2-chloroethyl vinyl ether (CEVE). NPM is among the most strongly electrophilic of the common olefinic monomers (Alfrey-Price *e* parameter = +3.24[16]), and EDA complexes have been implicated in its copolymerizations with styrene and with vinyl ethers.[4-6,17-21] NPM and its adducts are quite stable, so that accurate mass balances can be accomplished without undesirable product losses. Selection of the 1-butyl and benzyl radicals

[†] Present address: 3M Company, 201-3E-03 3M Center, St. Paul, MN 55144-1000.

[‡] Present address: Aristech Chemical Corporation, One Tech Center Drive, Monroeville, PA 15146.

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was motivated by the large difference in the reactivities of the two species: 1-butyl adds to typical olefins at a rate at least 1000-fold greater than that characteristic of the benzyl radical.[22,23] Because we intend to address in a very general way the question posed at the outset of this section, it is imperative that we examine a variety of model systems of widely differing reactivities.

This work constitutes part of our more general use of model reactions to address mechanistic issues in radical copolymerization.[24-26] Portions have been reported in preliminary form.[27,28]

Experimental Section

Materials. Acetic anhydride (Gold Label), aniline (Gold Label), benzylmagnesium chloride (2.0 M in tetrahydrofuran), butyllithium (2 M in hexane), ethyl 2-benzylacetoacetate, ethyl chloroacetate, mercuric bromide, and 2,2,6,6-tetramethylpiperidine were purchased from Aldrich Chemical Co. and used as received. Iodine and sodium acetate were obtained from Fisher Scientific Co. and used without purification. Sodium borohydride, diisopropylamine, and mercuric chloride were used as received from Alfa Chemical Co. 1-Bromobutane (Aldrich) was distilled (bp 100–104 °C). 2-Chloroethyl vinyl ether (Aldrich) was distilled from CaH_2 (bp 109 °C). Hydrocinnamic acid (Aldrich) was recrystallized from hot water (mp 47 °C). Methylene chloride (Fisher) was distilled from CaH_2 (bp 40 °C). *N*-Phenylmaleimide (Aldrich) was recrystallized from cyclohexane (mp 85 °C). Styrene (Aldrich) was distilled from CaH_2 (bp 50 °C (30 mmHg)). Tetrahydrofuran (Fisher) was distilled from $LiAlH_4$ (bp 67 °C).

Preparations. 1-Butylmercuric Bromide (BuHgBr). 1-Butylmercuric bromide was prepared by an adaptation of the method of Slotta and Jacobi.[29] To 3 g (123 mmol) of Mg in 25 mL of anhydrous ether was added 1 mL of 1-bromobutane and a few crystals of iodine. The flask was heated slightly to start the reaction. Once the reaction was started, the remaining alkyl bromide (16.4 g, 120 mmol) was added dropwise. After 20 min, the reaction mixture was heated to reflux for 1 h. The resulting Grignard reagent was filtered over glass wool under N_2 into a three-necked round-bottomed flask. Over a period of 45 min, 50 g (139 mmol) of $HgBr_2$ was added; the reaction mixture was shaken after each addition. After the addition was complete, the reaction was refluxed for 90 min and cooled to room temperature. Water (20 mL) was added very slowly, and the mixture was then washed three times with 2 N HCl. The ether layer was dried over $MgSO_4$ and the ether subsequently removed on the rotary evaporator. The resulting solid was recrystallized twice from cyclohexane and dried in vacuo to yield 35 g (86%) of 1-butylmercuric bromide; mp 123–124 °C (lit.[29] mp 136 °C; lit.[30] 129 °C). Anal. Calcd for C_4H_9HgBr: C, 14.2; H, 2.7. Found: C, 14.3; H, 2.6. ^1H NMR (300 MHz, CD_2Cl_2): δ 0.9 (t, 3 H), 1.4 (q, 2 H), 1.7 (q, 2 H), 2.1 (t, 2 H).

Benzylmercuric Chloride (BzHgCl). A dry 500-mL round-bottomed flask was charged with 100 mL of 2 M (0.2 mol) benzylmagnesium chloride in THF. Small portions of 54.3 g (0.2 mol) of mercuric chloride were added at such a rate as to keep the solvent from refluxing. When addition was complete, mixing was continued for 5 h longer. The product was isolated by pouring the reaction mixture into 1 L of dilute HCl. The resulting precipitate was filtered and recrystallized from chloroform to yield 54.2 g (83%) of benzylmercuric chloride; mp 101–102 °C (lit.[31] mp 104–105 °C). Anal. Calcd for C_7H_7HgCl: C, 29.7; H, 2.2. Found: C, 29.9; H, 2.2. IR (KBr, cm^{-1}): 3060, 3020, 2980, 2930, 1950, 1880, 1815, 1605, 1445, 1410, 1105, 1045, 745, 680. ^1H NMR (200 MHz, $CDCl_3$): δ 7.2 (m, 5 H), 3.2 (s, 2 H).

***N*-Phenyl-2-butylsuccinimide.** To a solution of 0.44 g (2.54 mmol) of NPM and 0.57 g (1.69 mmol) of 1-butylmercuric bromide in 5 mL of CH_2Cl_2 was added a solution of 0.128 g (3.38 mmol) of $NaBH_4$ in 0.5 mL of H_2O. When no further evolution of gas was apparent, the mixture was analyzed by gas chromatography (9-ft stainless-steel column packed with 3% SE-30 on 80/100 Supelcoport; column temperature, 180 °C; He flow, 50 mL/min) to monitor the disappearance of 1-butylmercuric bromide. In two subsequent additions, 0.06 and 0.04 mL of a 6.65 M solution of $NaBH_4$ in H_2O were added to the reaction mixture. After the second addition, no BuHgBr was detected. The solution was then filtered over $MgSO_4$ to remove water. Kugelrohr distillation followed by preparative thin-layer chromatography (3:1 CH_2Cl_2/petroleum ether) yielded 30 mg (10%) of *N*-phenyl-2-butylsuccinimide, mp 59 °C. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.7; H, 7.4; N, 6.1. Found: C, 72.2; H, 7.3; N, 5.8. ^1H NMR (300 MHz, CD_2Cl_2): δ 0.9 (t, 3 H), 1.2–2.0 (br, 10 H), 2.6 (m, 1 H), 2.9 (m, 1 H). MS: *m/e* 231.

Diethyl 2-Benzylsuccinate. A 300-mL 3-necked flask was equipped with a reflux condenser and dropping funnel. To the flask was charged under N_2 75 mL of ethanol freshly distilled from sodium ethoxide. Sodium (1.05 g, 45 mmol) was then dissolved in the ethanol, and ethyl 2-benzylacetoacetate (10 g, 45 mmol) was added dropwise to the reaction mixture with constant stirring. Ethyl chloroacetate (5.6 g, 0.45 mol) was then added over a 5-min period, and the solution was heated to reflux until neutral to pH test paper. The precipitated sodium chloride was filtered off and the filtrate distilled, with the highest boiling fraction (130–150 °C (0.5 mmHg)) kept as diethyl 2-benzylsuccinate, a very viscous yellow oil, yield 6.3 g (47%). IR (neat, cm^{-1}): 3000, 2940, 1740, 1610, 1375, 1180, 1030, 745, 700. ^1H NMR (80 MHz, $CDCl_3$): δ 7.2 (m, 5 H), 4.10 (q, 2 H), 4.15 (q, 2 H), 3.5–2.5 (m, 5 H), 1.15 (t, 3 H), 1.20 (t, 3 H).

2-Benzylsuccinic Acid. A mixture of 3 g (11 mmol) of diethyl 2-benzylsuccinate and 50 mL (150 mmol) of 3 M aqueous sodium hydroxide was heated to reflux for 20 h. The mixture was then cooled and acidified to pH 2 with concentrated HCl and the resultant precipitate was collected by filtration. The product was recrystallized from hot water to yield 2.0 g (87%) of 2-benzylsuccinic acid, mp 156–158 °C (lit.[32] mp 160 °C).[32] IR (KBr, cm^{-1}): 3500–2500 (br), 2900, 1700, 1405, 1290, 1220, 895, 745, 690. ^1H NMR (80 MHz, acetone-d_6): δ 7.2 (s, 5 H), 1.9–3.2 (m, 5 H).

2-Benzylsuccinic Anhydride. In a dry N_2 atmosphere, 2 g (10 mmol) of 2-benzylsuccinic acid and 40 mL of acetic anhydride were heated to reflux for 2 hr. The solution was fractionally distilled, and 1.9 g (100%) of the product, 2-benzylsuccinic anhydride, solidified in the receiving flask (bp 185 °C (2 mmHg); mp 94–95 °C (lit.[29] mp 95–97 °C)). IR (KBr, cm^{-1}): 3030, 2940, 1850, 1780, 1225, 1050, 900, 790. ^1H NMR (80 MHz, $CDCl_3$): δ 7.2 (m, 5 H), 3.75–2.6 (m, 5 H).

***N*-Phenyl-2-benzylsuccinimide.** 2-Benzylsuccinic anhydride (1.9 g, 10 mmol) was dissolved with stirring in a minimum volume of THF at room temperature. Aniline (1 mL, 11 mmol) was added all at once. Stirring was continued for an additional hour and the solution poured into 100 mL of diethyl ether. The resulting precipitate was collected by filtration and placed in a round-bottomed flask with 50 mL of acetic anhydride and 250 mg of sodium acetate. The mixture was heated to reflux for 2 h and cooled to room temperature. The resulting crystals were collected and recrystallized from diethyl ether to give 1.5 g (60%) of *N*-phenyl-2-benzylsuccinimide, mp 128–129 °C (lit.[33] mp 128–130 °C). IR (KBr, cm^{-1}): 3010, 2910, 2960, 1890, 1690, 1605, 1380, 1175, 725, 685. ^1H NMR (80 MHz, $CDCl_3$): δ 7.2 (m, 10 H), 2.5–3.5 nm, 5 H).

2,3-Dibenzylsuccinic Acid. A 500-mL round-bottomed flask equipped with a septum-capped dropping funnel was flushed with dry N_2 and charged with 9.4 g (93 mmol) of diisopropylamine and 200 mL of dry THF. The mixture was cooled to 0 °C, and 46.5 mL (93 mmol) of 2 M butyllithium in hexane was added dropwise. The solution was then cooled to −78 °C, and a solution of 7.0 g (47 mmol) of hydrocinnamic acid in 20 mL of THF was added dropwise. When addition was complete, mixing was continued at −78 °C for 1 h and the reaction mixture was warmed to room temperature over a 3-h period. The septum was then quickly replaced with a tubing adaptor to which was attached a thick-walled rubber tube leading to a dry ice trap and then to a Firestone valve, which was in turn supplied with a high vacuum source and a dry N_2 source. The Firestone valve was opened to the vacuum, and the solvent and diisopropylamine were removed from the reaction flask to leave the dilithium salt of hydrocinnamic acid as an off-white precipitate. The Firestone valve was then opened to the N_2 source, and the reaction vessel was filled with dry N_2. The tubing adaptor was removed and the septum quickly replaced. Another 50 mL of THF was added, and again the flask was cooled to −78 °C. Finally, a solution of 5.9 g (23 mmol) of iodine in 20 mL of THF was added dropwise, and the reaction mixture was stirred for 24 h at room temperature. The solution was then

poured into 150 mL of water, and the water was acidified to pH 2 with concentrated HCl. The resulting precipitate was collected by filtration and recrystallized from diethyl ether to give 5.6 g (80%) of 2,3-dibenzylsuccinic acid, mp 164–167 °C. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.5; H, 6.1; O, 21.4. Found: C, 72.0; H, 6.2; O, 22.0. IR (KBr, cm^{-1}): 3700–2800 (br), 1700, 1600, 1390, 1230, 1210, 880, 720, 680. ^1H NMR (80 MHz, acetone-d_6): δ 7.2 (s, 10 H), 3.25–3.0 (m, 6 H).

2,3-Dibenzylsuccinic Anhydride. A mixture of 2.0 g (6.7 mmol) of 2,3-dibenzylsuccinic acid and 50 mL of acetic anhydride was heated to reflux for 2 days under N_2. Excess acetic anhydride was removed by high vacuum rotary evaporation to leave 1.9 g (100%) of 2,3-dibenzylsuccinic anhydride as a brown precipitate, mp 110–114 °C. IR (KBr, cm^{-1}): 3060, 3020, 2920, 1840, 1770, 1600, 1230, 930, 910, 740, 690. ^1H NMR (80 MHz, $CDCl_3$): δ 6.95–7.45 (m, 10 H), 2.6–3.25 (m, 6 H).

2,3-Dibenzylsuccinic Acid Monophenylamide. 2,3-Dibenzylsuccinic anhydride (1.9 g, 6.7 mmol) was dissolved in stirring THF to which was added all at once 1 mL (11 mmol) of aniline. Stirring was continued for an additional hour, and the solution was poured into 100 mL of diethyl ether. The resulting precipitate was collected by filtration to yield 2.5 g (100%) of 2,3-dibenzylsuccinic acid monophenylamide, mp 181–184 °C. IR (KBr, cm^{-1}): 3400–2200 (br), 3280, 3020, 2420, 1695, 1950, 1880, 1650, 1600, 1530, 1560, 1435, 1230, 730, 680. ^1H NMR (80 MHz, acetone-d_6): δ 7.3 (m, 15 H), 4.5 (s, 1 H), 2.25–3.5 (m, 6 H).

***N*-Phenyl-2,3-dibenzylsuccinimide.** A mixture of 50 mL of acetic anhydride, 50 mg of sodium acetate, and 2.5 g (6.7 mmol) of 2,3-dibenzylsuccinic acid monophenylamide was heated to reflux for 60 h under N_2. The reaction mixture was allowed to stand at room temperature overnight, and the resulting crystals of *N*-phenyl-2,3-dibenzylsuccinimide were collected and recrystallized from diethyl ether to yield 640 mg (27%) of product, mp 188–190 °C. Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.3; H, 6.0; N, 3.9; O, 9.0. Found: C, 81.1; H, 5.8; N, 4.0; O, 9.1. IR (KBr, cm^{-1}): 3020, 3060, 2420, 1695, 1600, 1485, 1385, 1180, 730, 690, 645. ^1H NMR (300 MHz, $CDCl_3$): δ 7.3 (m, 15 H), 2.8–3.5 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 36.2, 45.8; 126.0, 127.0, 128.2, 128.9, 137.5, 179.1.

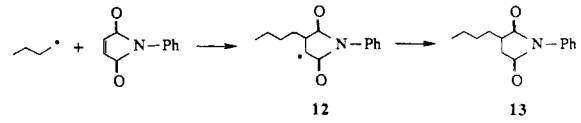
Epimerization of *N*-Phenyl-2,3-dibenzylsuccinimide. In a 10-mm diameter NMR tube was placed ca. 70 mg of *N*-phenyl-2,3-dibenzylsuccinimide. The compound was dissolved in 2 mL of $CDCl_3$, and a ^{13}C NMR spectrum was recorded. The solution was then placed in a 10-mL round-bottomed flask, and the solvent was removed by rotary evaporation. Dry THF and 3 drops of 2,2,6,6-tetramethylpiperidine were added, and the flask was fitted with a septum-capped reflux condenser and placed in an oil bath maintained at 60 °C. The solution was kept at 60 °C under dry N_2 for 18 h. Solvent and base were then removed by rotary evaporation, the residue was redissolved in 2 mL of $CDCl_3$, and a second ^{13}C NMR spectrum was recorded.

Monomer Mass Balance Experiments. General Considerations. Gas chromatographic analyses were performed on a Varian Series 1400 gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3380A digital integrator. Reaction products were identified by coinjection of reaction mixtures with authentic samples of compounds **13**, **14**, and **15**. Peak areas were converted to product yields on the basis of response factors determined by injection of standard solutions of NPM and each of the expected products.

BuHgBr–NPM–CEVE.[27] In a typical reaction 0.0445 g (0.257 mmol) of NPM and 0.0368 g (0.300 mmol) of CEVE were added to 0.078 g (0.231 mmol) of BuHgBr in 0.85 mL of CH_2Cl_2. To this solution at room temperature was added 4.54 mg (0.12 mmol) of $NaBH_4$ in 0.1 mL of H_2O. After 30 min, elemental Hg was separated, and the reaction mixture was analyzed by gas chromatography and gas chromatography/mass spectrometry (GC/MS) (9-ft stainless-steel column, 3% SE-30 on 80/100 Supelcoport; column temperature, 100 °C for 10 min, programmed to 250 °C; He flow, 50 mL/min). In some experiments, *tert*-butylbenzene was added as an internal chromatographic standard.

BuHgBr–NPM–Styrene.[28] In a typical reaction, 0.045 g (0.260 mmol) of NPM and 0.03 g (0.288 mmol) of styrene were added to 0.08 g (0.237 mmol) of BuHgBr in 1 mL of CH_2Cl_2. To this solution at room temperature was added 0.1 mL of a 6.8 M aqueous $NaBH_4$ solution. After 30 min, elemental Hg was separated and the reaction mixture was analyzed by gas chromatography (8-ft stainless-steel column packed with DC 200 HiPlate, column temperature, 120–185 °C, programmed temperature rate 30 °C/min after 1 min; N_2 flow rate, 30 mL/min). *tert*-Butylbenzene was added as an internal chromatographic standard.

Scheme III



12 13

BzHgCl–NPM–CEVE. In a typical procedure, 80 mg (0.24 mmol) of benzylmercuric chloride and 47 mg (0.27 mmol) of *N*-phenylmaleimide were charged to a glass tube, which was capped with a septum and purged with purified N_2. 2-Chloroethyl vinyl ether (28 mg, 0.28 mmol, prepurged with N_2), 10 μL of 1-phenylhexane (internal chromatographic standard) and 1.0 mL of N_2-purged methylene chloride were then added. The starting reaction mixture was analyzed by gas chromatography, and then 0.5 mL of 0.1 M aqueous $NaBH_4$ was added by syringe. After 30 min, elemental Hg was removed by filtration and the final reaction mixture was analyzed by gas chromatography (6-ft brass column packed with 3% SE-30 on 100/120 Varaport; column temperature, 150 °C for 6 min, programmed at 30 °C/min to 250 °C; He flow rate, 30 mL/min).

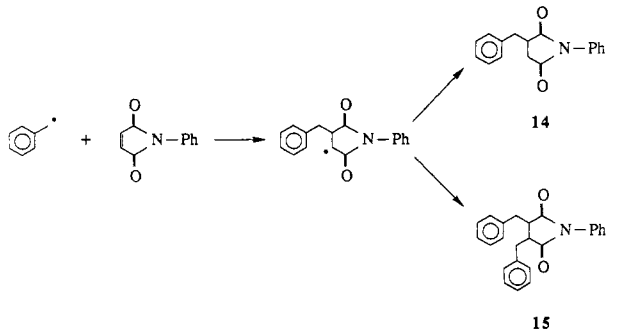
BzHgCl–NPM–Styrene. In a typical experiment, 66.1 mg (0.20 mmol) of benzylmercuric chloride and 38.4 mg (0.22 mmol) of *N*-phenylmaleimide were charged to a glass tube. The tube was capped with a septum, purged with purified N_2, and charged via syringe with 0.321 g (0.31 mmol) of N_2-purged styrene, 10 μL of 1-phenylhexane (internal chromatographic standard), and 1.0 mL of N_2-purged methylene chloride. The starting reaction mixture was analyzed by gas chromatography and then 0.5 mL of 0.1 M aqueous $NaBH_4$ was added by syringe. After 30 min, elemental Hg was removed by filtration and the final reaction mixture was analyzed by gas chromatography under conditions listed in the preceding section.

Measurements. ^1H NMR spectra were recorded at 300 MHz on a Varian XL-300 spectrometer, at 200 MHz on a Varian XL-200 spectrometer, and at 80 MHz on a Varian CFT-20 spectrometer. ^{13}C NMR spectra were recorded with broad-band decoupling on a Varian XL-200 instrument. Infrared spectra were obtained on Perkin-Elmer spectrophotometers, Model 283, 580, or 1320. Solid samples were analyzed as KBr pellets; liquids were run neat between NaCl plates. Line positions were calibrated by comparison with the 1601 cm^{-1} absorption band in polystyrene. Melting points were obtained either on a Thomas-Hoover capillary apparatus or on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

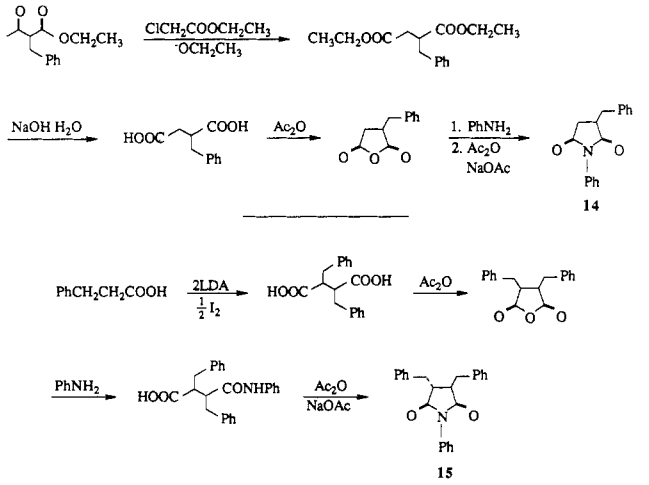
Results and Discussion

The nucleophilic character of simple alkyl radicals[34] ensures that both the 1-butyl and benzyl radicals will add much more rapidly to NPM than to either styrene or CEVE. The most instructive application of the trapping method outlined in Scheme I, therefore, is to perform a careful mass balance on NPM, i.e., to determine accurately the yields of all of the NPM-derived products of the reaction. For 1-butyl, simple addition to NPM followed by hydrogen-atom transfer to the adduct **12** affords 2-butyl-*N*-phenylsuccinimide (**13**) as essentially the sole product (Scheme III). On the other hand, our previous use[35] of the mercury method to examine the benzyl radical revealed a potential complication, in that certain adduct radicals were found to be trapped both by hydrogen-atom transfer and by transfer of a benzyl fragment. Although the fraction of radicals trapped by benzyl-fragment transfer generally declined with increasing electrophilicity of the radical center (from ca. 45% for the styryl adduct to ca. 6% for that derived from methyl acrylate), it appeared likely that simple addition of the benzyl radical to NPM would lead not only to *N*-phenyl-2-benzylsuccin-

Scheme IV



Scheme V

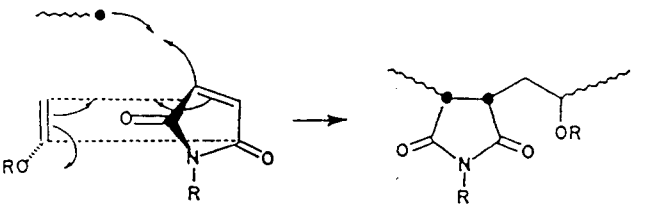


imide (14) but to the 2,3-dibenzyl product 15 as well (Scheme IV). We therefore prepared both 14 and 15 by independent routes (Scheme V), in order to provide pure samples for use in the development of methods for reliable, quantitative chromatographic detection of each of the likely products of benzyl radical addition. Recrystallization from diethyl ether afforded each of the products 14 and 15 in >99% purity by gas chromatography. Failure of 15 to epimerize under treatment with 2,2,6,6-tetramethylpiperidine was taken as evidence for formation of the trans isomer.

NPM–CEVE. The radical copolymerization of NPM and CEVE in CH_2Cl_2 provides nearly equimolar copolymers over a wide range of feed compositions.[4-6] Careful analysis of the carbonyl region of the ^{13}C NMR spectrum shows, however, that the microstructure of the copolymer changes with the monomer feed ratio, despite the near constancy of the copolymer composition. On the basis of epimerization experiments and spectral comparisons with model compounds, Olson and Butler have suggested that the microstructural change arises from a variation in the fraction of succinimidyl units incorporated into the copolymer in a cis configuration. According to their assignments, the fraction of cis units decreases with increasing mole fraction of NPM in the feed. They propose that the cis geometry is a consequence of propagation via the mechanism shown in Scheme VI: a concerted addition of a 1:1 monomer complex to the CEVE-terminated macroradical, in which radical attack occurs on the face of NPM that lies syn to the vinyl ether. The decrease in the cis fraction with increasing [NPM]/[CEVE] is then a consequence of an increase in the ratio of "free" NPM to that complexed with CEVE.

This proposal is nearly ideally suited to experimental test via the trapping method outlined in Scheme I. As discussed above, simple alkyl radicals generated by reductive demercuration should attack NPM almost exclusively at the expense of the vinyl ether; the question is then: *Is the NPM-derived radical trapped by CEVE or by transfer of a hydrogen atom (or benzyl fragment)*? Products 13-15 simply cannot arise via concerted complex addition, so that efficient formation of these products rules out such a mechanism.

Scheme VI



We have reported in preliminary form the results of trapping experiments in which the 1-butyl radical was generated in CH_2Cl_2 solutions of NPM and CEVE.[27] We selected conditions of concentration and temperature similar to those under which Olson and Butler found a relatively large fraction (ca. 0.8) of *cis*-succinimidyl units, i.e., conditions under which concerted addition is proposed to account for the consumption of a substantial fraction of NPM. We further verified that the presence of an aqueous phase (used in our experiments to introduce $NaBH_4$) did not affect the compositions or the ^{13}C NMR spectra of copolymers prepared under these conditions.

The results of these trapping experiments were unequivocal; 97 ± 7% of the reacted NPM was recovered as *N*-phenyl-2-butylsuccinimide (13), regardless of the conversion of NPM. Thus within experimental error, NPM was consumed quantitatively by simple addition and subsequent hydrogen-atom transfer; concerted complex addition was negligible.

We cited in our preliminary paper a number of concerns about this result, chief among them the adequacy of 1-butyl as a model of the CEVE-terminated macroradical proposed as the chain carrier by Olson and Butler. In fact, 1-butyl may be a better model than intuition would suggest. By plotting the rates of addition of the cyclohexyl radical to a series of olefins vs the Alfrey-Price *Q* and *e* parameters of those olefins, Giese and Meixner were able to assign an *e* parameter of −1.9 to cyclohexyl.[14] This is surprisingly similar to the value of *e* (−1.8) assigned to isobutyl vinyl ether[14] on the basis of this radical copolymerization behavior. Although we might expect the 1-butyl radical to be slightly less nucleophilic than cyclohexyl,[34] the difference is not expected to be large.

The α-alkoxy substituent on the CEVE-terminated macroradical would be expected to stabilize the radical center. Since our initial attempts to prepare (alkoxymethyl)mercuric halides were unsuccessful,[36] we chose instead the benzyl radical as a prototypical radical of reduced reactivity. Generation of the benzyl radical by borohydride reduction of benzylmercuric chloride in CH_2Cl_2 solutions of NPM and CEVE gave as major products bibenzyl and *N*-phenyl-2-phenylsuccinimide (14); *N*-phenyl-2,3-dibenzylsuccinimide (15) was formed in smaller amounts. Table I summarizes the results of seven such trapping experiments and compares (in the last column) the sum of the yields of 14 and 15 with the amount of NPM consumed. The results are consistent with those discussed above for the addition of 1-butyl to NPM; on average 106 ± 8% of the reacted NPM appears in the simple addition products. There is no evidence of concerted complex addition.

NPM–Styrene. Previous investigations of the copolymerization of NPM and its derivatives with styrene

Table I
Consumption of NPM by Benzyl Radical in the Presence of CEVE[a]

$[BzHgCl]_0$[b]	$[NPM]_0$[c]	$[CEVE]_0$[d]	$[NPM]_f$[e]	$[14]_f$[f]	$[15]_f$[g]	$([14]_f + [15]_f)/([NPM]_0 - [NPM]_f)$,[h] %
0.244	0.270	0.279	0.139	0.132	0.011	109 ± 8
0.110	0.205	0.206	0.129	0.073	0.004	101 ± 5
0.111	0.055	0.057	0.029	0.025	0.004	113 ± 8
0.217	0.213	0.268	0.107	0.104	0.008	106 ± 10
0.191	0.189	0.250	0.098	0.077	0.006	91 ± 4
0.150	0.153	0.201	0.090	0.063	0.004	106 ± 11
0.133	0.131	0.177	0.083	0.052	0.004	115 ± 12

[a] Conditions: solvent, CH_2Cl_2; room temperature; $[NaBH_4]_0$ = 0.1 M. [b] Concentrations reported in moles/liter. [c] Initial NPM concentration. [d] Initial CEVE concentration. [e] Final NPM concentration. [f] Final *N*-phenyl-2-benzylmaleimide (**14**) concentration. [g] Final 2,3-dibenzyl-*N*-phenylmaleimide (**15**) concentration. [h] Mean ± one standard deviation based on 3–4 determinations.

Table II
Consumption of NPM by Benzyl Radical in the Presence of Styrene[a]

$[BzHgCl]_0$[b]	$[NPM]_0$[c]	$[ST]_0$[d]	$[NPM]_f$[e]	$[14]_f$[f]	$[15]_f$[g]	$([14]_f + [15]_f)/([NPM]_0 - [NPM]_f)$,[h] %
0.201	0.223	0.316	0.120	0.100	0.005	102 ± 5
0.203	0.222	0.309	0.185	0.029	0.001	81 ± 3
0.202	0.284	0.302	0.123	0.129	0.010	86 ± 7
0.200	0.222	0.281	0.110	0.099	0.005	93 ± 6
0.198	0.217	0.266	0.112	0.090	0.006	91 ± 5
0.199	0.223	0.286	0.134	0.067	0.004	80 ± 3
0.203	0.280	0.300	0.140	0.123	0.014	98 ± 4

[a] Conditions: solvent, CH_2Cl_2; room temperature; $[NaBH_4]_0$ = 0.1 M. [b] Concentrations reported in moles/liter. [c] Initial NPM concentration. [d] Initial styrene concentration. [e] Final NPM concentration. [f] Final *N*-phenyl-2-benzylmaleimide (**14**) concentration. [g] Final *N*-phenyl-2,3-dibenzylmaleimide (**15**) concentration. [h] Mean ± one standard deviation based on 3–4 determinations.

have been interpreted as providing evidence both for[17-21] and against[37,38] the participation of 1:1 monomer complexes. Neither Barrales-Rienda[37] nor Yoshihara[38] were able to identify appreciable charge-transfer bands in the UV spectra of styrene–NPM mixtures. On the other hand, Rzaev and Dzahafarov[19,20] assert that "the predominant mechanism [of the copolymerization of styrene and NPM] was by addition of the charge-transfer complex of the monomers to the macroradical". Most recently, Elsabee and co-workers have analyzed the radical copolymerization of styrene and *N*-(2-chlorophenyl)maleimide according to the kinetic scheme of Georgiev and Zubov,[39] and they ascribe about 65% of the overall rate to reactions of the complex.[21,40]

We have reported previously that generation of the 1-butyl radical by hydride reduction of 1-butylmercuric bromide in CH_2Cl_2 solutions of styrene and NPM provides *N*-phenyl-2-butylsuccinimide (**13**) as the sole major product.[28] In a series of trapping experiments run at room temperature with the initial concentrations of styrene and NPM fixed at 0.27–0.32 M and 0.21–0.26 M, respectively, the average yield of **13** was 87 ± 8%, and we were unable to identify any other NPM-derived products of the reaction. Concerted addition of the 1:1 EDA complex does not constitute a major pathway for monomer consumption under these conditions.

The benzyl radical constitutes an excellent model of the styryl-terminated macroradical that is a likely chain carrier in the copolymerization of styrene and NPM. Table II summarizes the results of seven trapping experiments on the benzyl radical, in which the combined yields of the simple addition products **14** and **15** are compared with the amounts of NPM consumed. Under these conditions (room temperature; CH_2Cl_2; $[styrene]_0$ = 0.27–0.32 M; $[NPM]_0$ = 0.22–0.28 M), 90 ± 5% of the reacted NPM appears in the simple adducts. As before (ca. Table I), trapping of the intermediate NPM-derived radical occurs predominantly by transfer of a hydrogen atom, rather than a benzyl fragment; the ratio of products **14** and **15** is approximately 20.

Table III
Yields of Simple Addition Products from Reactions of Alkyl Radicals with NPM in Solutions of Donor Olefins[a]

radical	donor olefin	yield of simple adducts, %
1-butyl	CEVE	97 ± 7
1-butyl	styrene	87 ± 8
benzyl	CEVE	106 ± 8
benzyl	styrene	90 ± 5

[a] Yields are means of results presented in detail in Tables I and II and in the tables of ref 27 and 28.

The conditions of these experiments are similar, but not identical, to those of Elsabee and co-workers.[21] Elsabee used *N*-(2-chlorophenyl)maleimide, rather than the parent NPM, and the temperature (60 °C), solvent ($CHCl_3$) and monomer concentrations ($[styrene]_0$ = 0.6 M, $[CPM]_0$ = 0.4 M) employed in their work are all slightly different from ours. One can speculate that the higher dielectric constant of CH_2Cl_2, and the lower monomer concentrations used in our work, should reduce complex formation and participation. On the other hand, our experiments were run at 25 °C rather than 60 °C, a factor that might be expected to promote participation of the EDA complex.[4-6] Recognizing these differences, we assert that our results argue against concerted complex addition as an important means by which NPM is consumed in reactions with benzylic radicals.

Conclusions. Table III summarizes the results of four sets of trapping experiments, in which two simple alkyl radicals (1-butyl and benzyl) of greatly differing reactivity were generated in mixtures of the acceptor olefin NPM (e = +3.24[16]) and either of two donor olefins, styrene (e = −0.8[16]) and CEVE (e = −1.58[16]). The table lists the fractions of the reacted NPM that were recovered in the form of the products of simple addition followed by transfer of a hydrogen atom or benzyl fragment. In each case, the yield of simple addition products is nearly quantitative and argues against concerted addition of a 1:1 complex of the monomers as an important pathway for

monomer consumption.

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Hydrodynamic Chromatography as a Probe of Polymer Dynamics during Flow through Porous Media

David A. Hoagland* and R. K. Prud'homme

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544.
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ABSTRACT: Hydrodynamic chromatography (HDC) of both flexible and stiff macromolecules provides measurements of molecular size that depend strongly on column flow rate.[1,2] This flow rate dependence is explained in terms of deformation and orientation of simple molecular models in steady uniaxial elongation, an idealized flow with many, but not all, of the properties required to describe the real flow of polymer solutions in complex porous media. The polymer/flow description discussed here follows from earlier theories for the anomalous "excess" pressure drop/flow rate behavior of low-concentration polymer solutions in porous media.

Introduction

Polymer solutions exhibit pronounced non-Newtonian flow behavior in porous media containing small converging and diverging flow channels. With flexible polymers these effects have been attributed to flow-induced molecular stretching in the Lagrangian unsteady elongational flows found in convering flow passages. Direct measurement of polymer deformation in small pores is exceedingly difficult; molecular stretching is normally inferred indirectly from pressure drop/flow rate data. Hydrodynamic chromatography offers a second probe of molecular shape in these complicated flows. The technique follows changes in molecular conformation via flow rate dependent elution volumes of molecules which are able to undergo extension and orientation by hydrodynamic stress.

Flow-induced stretching of a flexible polymer occurs when the chain is subjected to hydrodynamic forces greater in magnitude than the forces of chain relaxation arising from Brownian motion. Flows imposing hydrodynamic stresses sufficiently large for molecular deformation are terms "strong", while flows in which the polymer retains its equilibrium conformation are "weak".[3] The strength of a flow can often be correlated with its Deborah number, De. The Deborah number is defined as a ratio of the hydrodynamic forces to the Brownian forces or, equivalently, as the ratio of the relaxation time of the polymer

*Current address: Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003.

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