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Model Copolymerization Reactions. Determination of the Relative Rates of Addition of Styrene and Acrylonitrile to the Benzyl Radical

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ABSTRACT: Reductive demercuration of benzylmercuric chloride in CH_2Cl_2 solutions affords toluene and bibenzyl as major products in a ratio of ca. 4:3. In similar solutions that contain styrene and acrylonitrile, one obtains not only toluene and bibenzyl but also 1,3-diphenylpropane (**11**), 1,2,4-triphenylbutane (**12**), 4-phenylbutyronitrile (**13**), and 2-benzyl-4-phenylbutyronitrile (**14**). Each of these products can be rationalized on the basis of a reaction scheme in which addition of the benzyl radical to styrene or acrylonitrile is followed by trapping of the adduct by transfer of a hydrogen atom or a benzyl fragment. The product ratios **11**:**12** and **13**:**14** were found to be independent of reaction conditions within the range of conditions employed in this work. The relative rates of addition of styrene and acrylonitrile (k_S/k_A) were determined by analysis of relative product yields as a function of the relative starting concentrations of styrene and acrylonitrile. We find $k_S/k_A = 0.33 \pm 0.04$, a result that is consistent with the known selectivity of the 1-phenylethyl radical and that falls within the range of published reactivity ratios for styrene in its copolymerization with acrylonitrile. These results support the use of the mercury method as a source of simple, reliable models for the macroradicals involved in the growth of copolymer chains.

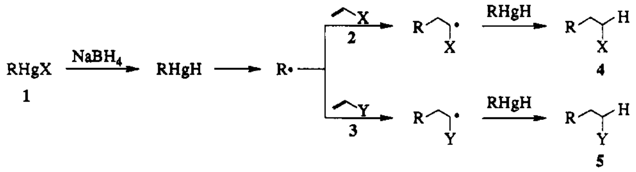
Introduction

The radical copolymerization of styrene and acrylonitrile merits special interest. On one hand, it is an important commercial process, and on the other, it offers special advantages in the study of the fundamentals of copolymerization mechanisms. In particular, Hill and coworkers have used the styrene (S)–acrylonitrile (A) system to demonstrate the power of sequence determination in discriminating among alternative kinetic descriptions of copolymerization processes.[1] On the basis of their sequence data, they conclude that this copolymerization, when run in the absence of solvent, is best described by a penultimate kinetic scheme with reactivity ratios $r_{SS} = 0.23$, $r_{AS} = 0.63$, $r_{AA} = 0.04$, and $r_{SA} = 0.09$.

We have also devoted some effort to the study of the copolymerization of styrene and acrylonitrile,[2-4] although our approach has been quite different. In 1985, we reported the results of an investigation of the effects of γ-substituents (i.e., analogues of penultimate units) on the selectivity of addition of simple alkyl radicals to styrene and acrylonitrile.[2] The results of these experiments were remarkably consistent with those of Hill and co-workers, in that we found a 3.5-fold depression in the relative rate of addition of acrylonitrile (k_A/k_S) upon replacement of a γ-phenyl group with a γ-cyano substituent on the attacking radical. The direct observation of a "penultimate effect" of this magnitude in this simple model system lends support to the penultimate model as a physically meaningful description of the copolymerization of styrene and acrylonitrile.

The alkyl radicals discussed in ref 2 were generated by reductive demercuration of the appropriate alkylmercuric bromides, according to Scheme I. This "mercury method" has been used extensively by Giese and co-workers to examine a range of questions about the reactivity of simple radicals.[5] Furthermore, Giese and Meixner[6] have demonstrated an excellent correlation of the relative rates of addition of a series of olefins to the cyclohexyl radical (generated by reductive demercuration) with the rates of addition of the same olefins to the styryl-terminated macroradicals that are involved in the propagation of radical copolymerizations. These results recommend the mercury method as a convenient source of model radicals for use in investigation of the mechanisms of radical copolymerization. We describe herein the use of the mercury method to determine the relative rates of addition of styrene and acrylonitrile to the benzyl radical, a plausible model of the styryl-terminated macroradicals involved in the growth of copolymer chains. The results lend further support to the use of the mercury method as an experimental probe of copolymerization behavior.

Scheme I



Experimental Section

Materials. Benzylmagnesium chloride (2 M in THF), *n*-butyllithium (1 M in hexanes), diethylene glycol, hydrazine monohydrate, hydrocinnamaldehyde, hydrocinnamonitrile, and phenylacetaldehyde were purchased from Aldrich Chemical Co. and used as received. Acrylonitrile (distilled from CaH_2 under dry N_2), benzyl bromide (distilled, bp 199 °C), (2-bromoethyl)benzene (distilled, bp 220 °C), 1,3-diphenylacetone (recrystallized from petroleum ether), dichloromethane (distilled from CaH_2 under dry N_2), and thionyl chloride (distilled, bp 79 °C from cotton-seed oil) were also obtained from Aldrich. Diisopropylamine, mercuric chloride, and sodium borohydride were used as received from Alfa Chemical Co. Tetrahydrofuran (THF, Fisher) was distilled (bp 67 °C) from lithium aluminum hydride. Quinoline was used as received from Fisher Scientific Co.

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 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 BzHgCl, mp 101–102 °C (lit. mp 104–105 °C).[7]

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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. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.2 (m, 5 H), 3.2 (s, 2 H).

1,3-Diphenylpropane. A mixture of 7.0 g (33 mmol) of 1,3-diphenylacetone, 3.74 g (67 mmol) of potassium hydroxide, 5.0 g (100 mmol) of hydrazine monohydrate, and 35 mL of diethylene glycol was placed in a 100-mL round-bottomed flask fitted with a fractionating column and still head. The mixture was heated with constant stirring to 240 °C until no more water or hydrazine was driven off; the temperature was then adjusted to 210 °C and maintained overnight. The mixture was cooled, taken up into 200 mL of water, and extracted with two 50-mL portions of benzene. The benzene layer was dried ($MgSO_4$) and stripped to yield after distillation [bp 135 °C (4 mm Hg)] 3.23 g (79%) of 1,3-diphenylpropane as a thin, yellow oil: IR (neat), cm^{-1}: 3080, 3030, 2930, 2855, 1600, 1450, 750, 690. ^{1}H NMR (80 MHz, $CDCl_3$): δ 7.2 (m, 10 H), 2.6 (t, 4 H), 1.9 (m, 2 H).

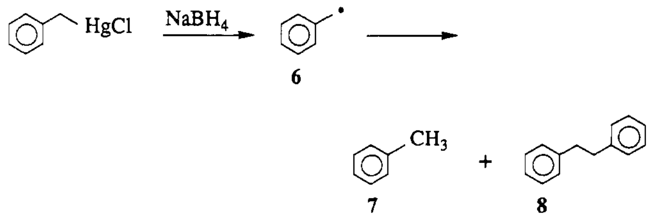
1,3,4-Triphenyl-2-butanone. In a 250-mL round-bottomed flask equipped with a dropping funnel, 24 mmol of lithium diisopropylamide (LDA) was prepared under dry N_2 in the following manner. At 0 °C, 2.43 g (24 mmol) of diisopropylamine and 30 mL of dry THF were charged to the flask. *n*-Butyllithium (24 mL of 1 M hexane solution, 24 mmol) was added dropwise and the solution was stirred for an additional 30 min before use. 1,3-Diphenylacetone (5 g, 24 mmol) in 15 mL of THF was added dropwise. The blood-red solution was stirred at 0 °C for an additional 30 min, whereupon 4.1 g (24 mmol) benzyl bromide was added over a 5-min period. After mixing at room temperature for 4 h, the product was isolated by taking the reaction mixture up in 300 mL of ether, washing with three 100 mL portions of water, and drying ($MgSO_4$). After removal of the ether, a solid remained which was recrystallized from 2:1 ether/petroleum ether to yield 3.9 g (54%) of 1,3,4-triphenyl-2-butanone, mp 76–7 °C (lit.[8] mp 76–77 °C). IR (KBr), cm^{-1}: 3060, 3020, 2960, 2860, 1950, 1880, 1740, 1605, 1495, 1455, 1110, 1060, 740, 690. ^{1}H NMR (80 MHz, $CDCl_3$): δ 6.5–7.2 (m, 15 H), 4.10 (t, 1 H), 3.65 (s, 2 H), 2.75-3.4 (m, 2 H).

1,2,4-Triphenylbutane. A mixture of 3.0 g (11 mmol) of 1,3,4-triphenyl-2-butanone, 1.20 g (22 mmol) of potassium hydroxide, 1.65 g (33 mmol) of hydrazine monohydrate, and 20 mL of diethylene glycol was placed in a 50-mL round-bottomed flask fitted with a fractionating column and a still head. The mixture was heated with constant stirring to 240 °C until no more water was driven off; the temperature was then adjusted to 210 °C and maintained overnight. The mixture was cooled, taken up into 50 mL of water, and extracted with two 50-mL portions of benzene. The benzene layer was dried ($MgSO_4$) and stripped to yield 1.8 g (57%) of 1,2,4-triphenylbutane as a very viscous oil of 98% purity by gas chromatography. IR (neat), cm^{-1}: 3080, 3030, 2925, 2860, 1945, 1875, 1810, 1605, 1495, 1455, 1070, 1025, 745, 690. ^{1}H NMR (80 MHz, $CdCl_3$): δ 7.2 (m, 15 H), 2.8 (m, 3 H), 2.4 (m, 2 H), 1.9 (m, 2 H).

2-Benzyl-4-phenylbutyronitrile. Under anhydrous N_2, 38 mmol of LDA in 50 mL of THF was prepared at 0 °C from 3.9 g (38 mmol) of diisopropylamine and 19 mL (38 mmol) of 2 M *n*-butyllithium as previously described. The reaction mixture was cooled to −78 °C, and 5 g (38 mmol) of hydrocinnamonitrile in 10 mL of THF was added all at once. Exactly 5 min later, a solution of 7.0 g (38 mmol) of (2-bromoethyl)benzene in 10 mL of THF was added over a 1-min period. The solution was stirred at −78 °C for an additional 3 h. The solution was warmed to room temperature, the precipitated lithium bromide filtered off, and the solvent removed by rotary evaporation. The residue, 2-benzyl-4-phenylbutyronitrile, was fractionally distilled four times on a Kugelrohr apparatus [oven temperature 140 °C (1 mmHg)] to obtain 96% purity by gas chromatography. The yield of distilled product was 307 mg (3%). IR (neat), cm^{-1}: 3045, 3010, 2910, 2210, 1950, 1970, 1800, 1600, 1485, 1440, 725, 680. ^{1}H NMR (80 MHz, $CDCl_3$): δ 7.25 (m, 10 H), 2.9 (m, 5 H), 1.9 (m, 2 H).

Determination of Relative Rates of Hydrogen and Benzyl Trapping. In a typical experiment, 33 mg (0.1 mmol) of BzHgCl was charged to a glass tube, which was closed with a rubber septum and purged with N_2. The tube was then further charged via syringe with 1 mL of N_2-purged dichloromethane and a precisely known quantity (ca. 10 mmol) of N_2-purged styrene or acrylonitrile. Finally, 0.5 mL of 0.1 M aqueous $NaBH_4$ was added via syringe. After 30 min at room temperature, the reaction mixture was separated from precipitated elemental mercury and analyzed by gas chromatography. For reaction mixtures that contained styrene, conditions were the following: 6 ft, $^1/_8$-in. o.d. column packed with 3% SE-30 on 100/120 Varaport; injector, 250 °C; detector, 250 °C; column, 240 °C; He 30 mL/min; flame ionization detection. For reaction mixtures that contained no styrene the conditions were as follows: 9 ft, $^1/_4$-in. o.d. column packed with 3% SE-30 on 80/100 Supelcoport; injector, 250 °C; detector, 250 °C; column, 240 °C; He 30 mL/min; flame ionization detection. Reaction products were identified by coinjection with authentic samples prepared by independent routes and quantitated on the basis of response factors determined by injection of mixtures of known composition.

Scheme II



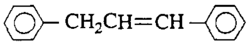
Competitive Addition of Styrene and Acrylonitrile to the Benzyl Radical. In a typical experiment, 33 mg (0.1 mmol) of BzHgCl was charged to a glass tube, which was closed with a rubber septum and purged with N_2. The tube was then further charged via syringe with precisely known quantities (ca. 1–5 mmol each) of N_2-purged styrene and acrylonitrile and finally with 1 mL of N_2-purged dichloromethane. Aqueous $NaBH_4$ (0.5 mL of a 0.1 M solution) was then added via syringe. After 30 min at room temperature, the reaction mixture was separated from precipitated elemental mercury and analyzed by gas chromatography (9 ft, $^1/_4$-in. o.d. column packed with 3% SE-30 on 80/100 Supelcoport; injector, 250 °C; detector, 250 °C; column, 180 °C; He 30 mL/min; flame ionization detection). Reaction products were identified by coinjection with authentic samples prepared by independent routes and quantitated on the basis of response factors determined by injection of mixtures of known composition.

Results and Discussion

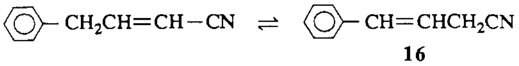
Treatment of CH_2Cl_2 solutions of BzHgCl with aqueous $NaBH_4$ at room temperature affords toluene and bibenzyl as major products in a ratio of ca. 4:3. Each of these products can be rationalized on the basis of a modification of Scheme I, in which the intermediate benzyl radical **6** is trapped by transfer of either a hydrogen atom (to yield toluene **7**) or a benzyl fragment (to yield bibenzyl **8**) (Scheme II).

The implications of Scheme II are clear with respect to the use of the mercury method to determine the relative rates of olefin addition to the benzyl radical (and, by inference, to other stabilized radicals as well): One must determine the relative yields not of two products, as with simple alkyl radicals (Scheme I), but rather of all four major products (e.g., **11–14**) of olefin addition and subsequent trapping (Scheme III).

An additional complication might conceivably arise if the benzyl-trapped products **12** and **14** result from radical coupling, rather than from S_H2 transfer of a benzyl fragment from mercury.[9] One might then anticipate some competitive formation of the disproportionation products **15** and **16** in addition to **11** and **14**. In order to address


$C_6H_5CH_2CH{=}CH{-}C_6H_5$

15


$C_6H_5CH_2CH{=}CH{-}CN \rightleftharpoons C_6H_5CH{=}CHCH_2CN$

16

Scheme III

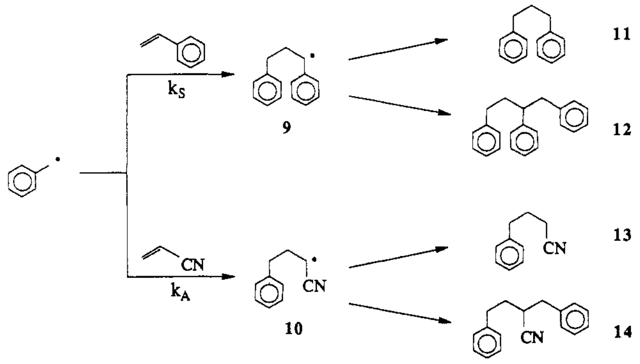


Table I
Relative Rates of Addition of Styrene and Acrylonitrile to the Benzyl Radical[a]

reaction	$[S]_0$,[b] M	$[A]_0$,[c] M	$[S]_0/[A]_0$	$[11]_f/[13]_f$[d,e]
1	3.73	1.26	2.96	0.66 ± 0.02
2	3.58	1.42	2.53	0.51 ± 0.12
3	3.34	1.66	2.02	0.43 ± 0.06
4	3.07	1.93	1.59	0.29 ± 0.01
5	2.51	2.49	1.00	0.21 ± 0.09
6	1.62	3.38	0.48	0.12 ± 0.03

[a] Conditions: 0.1 mmol of BzHgCl in 1 mL of dichloromethane; 0.5 mL of 0.1 M aqueous $NaBH_4$; 50-fold excess of total monomer relative to BzHgCl, room temperature. [b] Initial styrene concentration. [c] Initial acrylonitrile concentration. [d] Ratio of final concentrations of products 11 and 13. [e] Mean ± one standard deviation from three determinations.

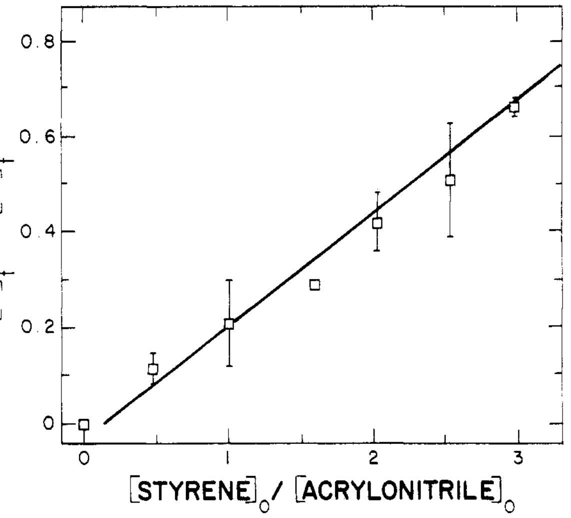


Figure 1. Ratio of products 11 and 13 as a function of the initial ratio of styrene and acrylonitrile in the reductive demercuration of BzHgCl in CH_2Cl_2.

this question, we prepared 15[10] and 16[11] (each as a mixture of isomers) and searched the products of competitive addition for evidence of disproportionation. None was found.[12] Quantitation of products 11–14 is thus sufficient for reliable determimation of the relative rates of olefin addition. Higher oligomers of styrene and acrylonitrile are precluded by the rapid capture of the initial adducts 9 and 10, and while the high trapping rate reduces the yields of 11–14 (by diverting most of the benzyl radicals to toluene and bibenzyl) the relative product yields are readily determined with the required accuracy and precision.

Routine quantitation of each of the products 11–14 proved to be inconvenient, as a result of the wide variation in boiling points. In contrast, determination of the relative yields of the hydrogen-trapped products 11 and 13 was straightforward. Thus it was of interest to determine the partitioning of each of the adducts 9 and 10 between the products of trapping by hydrogen and by benzyl fragments; if the ratios 11:12 and 13:14 are known *and independent of reaction conditions*, a simple determination of the ratio of products 11 and 13 is sufficient to determine the rate constant ratio k_S/k_A (Scheme III).

The ratio of products 11 and 12 was determined by reduction of BzHgCl in the presence of styrene alone and in solutions that contained increasing amounts of acrylonitrile. The ratio of products derived from styrene addition was independent of both the total monomer concentration and the relative concentrations of the monomers. We found in each case that 11:12 = 1.19 ± 0.08, which is quite consistent with the ca. 4:3 ratio of toluene and bibenzyl obtained in the absence of monomer. In similar fashion, the ratio of 13 to 14 was determined to be 5.26 ± 0.55, independent of reaction conditions over the range employed in this work.[13] Thus the simple quantitation of products 11 and 13 is sufficient to determine k_S/k_A.

Table I summarizes the results of a series of competitive additions of styrene and acrylonitrile to the benzyl radical, and Figure 1 presents a plot of the product ratio 11:13 versus the ratio of styrene to acrylonitrile in the initial reaction mixture. As expected, the plot is linear and passes near the origin. Correction of the slope of the best-fit line with the results of the H versus benzyl trapping experiments just described gives $k_S/k_A = 0.33 \pm 0.04$.

It is instructive to compare this ratio of rate constants with the published range of reactivity ratios (r_S) determined via radical copolymerization of styrene and acrylonitrile. The most recent critical summary of reactivity ratios[16] lists values of r_S from 0.27 to 0.54, and the best-fit terminal model of Hill and co-workers requires that r_S = 0.33.[1] The terminal model would suggest that our measured k_S/k_A should be similar to r_S, though one might expect some deviation as a result of the fact that the benzyl radical is primary while the styryl-terminated macroradical is secondary. In fact, we have determined k_S/k_A for the 1-phenylethyl radical,[3] the simplest secondary model, and we find the expected increase in selectivity ($k_S/k_A = 0.20 \pm 0.02$) in comparison with the benzyl radical. This value of k_S/k_A for 1-phenylethyl is in remarkably good agreement with the penultimate-model reactivity ratio r_{SS} (=0.23) reported by Hill. Thus we do not interpret our present results as evidence in favor of a terminal-model description of the copolymerization of styrene and acrylonitrile. On the contrary, the difference in k_S/k_A for the 1-phenylethyl and benzyl radicals is completely consistent with known differences in the selectivities of primary and secondary radicals.[17] The fact that the rate constant ratios were determined by very different chemical methods (end-group labeling for 1-phenylethyl versus the mercury method for benzyl) lends credibility to *each* of these techniques as useful models of radical copolymerization processes.

Conclusions

Reductive demercuration of BzHgCl in CH_2Cl_2 solutions of styrene and acrylonitrile allows accurate determination of the relative rates of addition of these two monomers to the benzyl radical. We obtain $k_S/k_A = 0.33 \pm 0.04$, a result that is consistent with the known selectivity of the 1-phenylethyl radical and that falls within the range of published reactivity ratios for styrene in its copolymerization with acrylonitrile. These experiments support the use of the mercury method as source of simple, reliable models for the macroradicals involved in the growth of copolymer chains.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Support of our research programs by a Presidential Young Investigator Award of the National Science Foundation is also gratefully acknowledged. NMR spectra were recorded in the University of Massachusetts NMR Laboratory, which is supported in part by the NSF Materials Research Laboratory at the university.

Registry No. 1,3-Diphenylpropane, 1081-75-0; 1,3-diphenylacetone, 102-04-5; 1,3,4-triphenyl-2-butanone, 62640-72-6; benzyl bromide, 100-39-0; 1,2,4-triphenylbutane, 116374-60-8; 2-benzyl-4-phenylbutyronitrile, 89873-50-7; hydrocinnamonitrile, 645-59-0; 2-(bromoethyl)benzene, 103-63-9; styrene, 100-42-5; acrylonitrile, 107-13-1; 4-phenylbutyronitrile, 2046-18-6; benzylmercuric chloride, 2117-39-7.

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(12) A reviewer has suggested that **15** and **16**, if formed, may be consumed by radical addition and may not be detected in our experiments. We would anticipate that the reduced activity of **15** and **16**, and the large excesses of acrylonitrile and styrene used in our experiments, would preclude significant interference from reactions of this kind.

(13) The partitioning of alkyl radicals between hydrogen-trapped and benzyl-trapped products appears to correlate with the electrophilicity of the radical. For example, radicals derived from addition to *N*-phenylmaleimide (for which the Alfrey-Price *e*-parameter is +3.24[14]) are trapped almost exclusively by hydrogen atom transfer.[15] We attribute the observed differences in ratios **11**:**12** and **13**:**14** to the differences in the electrophilicities of radicals **9** and **10**.

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Involvement of Analogues of Stilbene in Radical Polymerization: The Reactions of Arylstyrenes with Benzoyloxy Radical

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ABSTRACT: Styrene and methyl methacrylate have been polymerized at 60 °C in the presence of low concentrations of various arylstyrenes, $C_6H_5CH{=}CHAr$, using benzoyl-*carbonyl*-^{13}C peroxide as initiator; the arylstyrenes are regarded as analogues of stilbene. The benzoate end groups in the resulting polymers have been examined by ^{13}C NMR spectroscopy; many of them are found to be attached to units derived from the stilbene-like compounds, although only very small amounts of these additives are incorporated in the whole polymers. The relative reactivities toward the benzoyloxy radical of methyl methacrylate, styrene, and the *E* isomers of stilbene and its analogues derived from biphenyl, naphthalene, phenanthrene, and anthracene are approximately 0.12, 1, 6, 13, 14, 18, and 65, respectively.

Introduction

The trans (or *E*) isomer of stilbene (STL) has high reactivity towards the benzoyloxy radical; consequently, if methyl methacrylate (MMA) or styrene (STY) is polymerized at 60 °C with benzoyl peroxide (BPO) as initiator in the presence of STL at quite low concentration, many of the end groups in the resulting polymer consist of benzoate groups attached to units derived from STL.[1] The total incorporation of STL in the polymer is small; thus for its copolymerization with MMA (monomer 1), the monomer reactivity ratio r_1 exceeds 400 and r_2 is close to zero[2] so that a system in which [MMA]/[STL] is 100 gives rise to a polymer containing more than 4×10^4 MMA units for each in-chain STL unit and yet about 40% of the benzoate end groups are adjacent to STL units. The introduction of STL into MMA being polymerized with BPO leads to a marked increase in the ratio of benzoate to phenyl end groups without appreciable effect upon the overall composition of the polymer.[3] Although STL is so reactive toward the benzoyloxy radical, it is unreactive toward the 1-cyano-1-methylethyl radical derived from azobis(isobutyronitrile) (AIBN); this difference between the initiating radicals has been ascribed to steric effects.[1] A similar explanation has been given[4] to account for BPO being more effective than AIBN as an initiator for the polymerization of another 1,2-disubstituted monomer, viz., ethyl cinnamate.

The high reactivity toward the benzoyloxy radical is retained, and in some cases considerably enhanced, if substituents are introduced at the para positions in one or both of the phenyl rings of STL.[3,5] If k_m is the velocity constant for the reaction of the radical with MMA and k is that for the corresponding reaction of a STL-like substance, the values of k/k_m at 60 °C for STL and its 4-chloro-, 4,4′-dichloro-, 4-methoxy-, and 4-methoxy-4′-chloro- derivatives are 40, 90, 37, 300, and 230, respectively. Hetero-aromatic analogues of STL also react readily with benzoyloxy radical; in the case of 2-styrylthiophene, k/k_m at 60 °C exceeds 250.[6] These analogues may be useful for the preparation of polymers having functional groups very close to the ends of macromolecules; for this purpose, they offer an alternative to the use of special initiators.

The work referred to in the previous paragraphs has been extended to analogues of STL having one of the phenyl groups replaced by an aromatic hydrocarbon residue, i.e., arylstyrenes. The analogues used in the investigations now reported were 4-(2-phenylethenyl)-1,1′-biphenyl (Biph-STL), 1-(2-phenylethenyl)naphthalene