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.

References and Notes

(1) Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W. *Macromolecules* **1982**, *15*, 960.
(2) Jones, S. A.; Prementine, G. S.; Tirrell, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5275.
(3) Cywar, D. A.; Tirrell, D. A. *Macromolecules* **1986**, *19*, 2908.
(4) Prementine, G. S.; Tirrell, D. A. *Macromolecules* **1987**, *20*, 3034.
(5) For leading references, see: Giese, B. *Radicals in Organic Synthesis: Formation of Carbon*-Carbon Bonds; Pergamon: Oxford, 1986.
(6) Giese, B.; Meixner, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 206.
(7) Oesper, P. F.; Smyth, C. P. *J. Am. Chem. Soc.* **1942**, *64*, 173.
(8) Hauser, C. H.; Harris, T. M. *J. Am. Chem. Soc.* **1959**, *81*, 1154.
(9) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398.
(10) Raunio, E. K.; Bonner, W. A. *J. Org. Chem.* **1966**, *31*, 396.
(11) Prochazka, M.; Uchytil, B.; Zelinka, J. *Collect. Czech. Chem. Commun.* **1974**, *39*, 1342.
(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**.
(14) Greenley, R. Z. *J. Macromol. Sci., Chem.* **1980**, *A14*, 427.
(15) Prementine, G. S. Ph.D. Dissertation, Carnegie Mellon University, 1987.
(16) Greenley, R. Z. *J. Macromol. Sci., Chem.* **1980**, *A14*, 445.
(17) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753, and references therein.

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

(Naph-STL), 9-(2-phenylethenyl)phenanthrene (Phen-STL), and 9-(2-phenylethenyl)anthracene (Anth-STL). The experimental procedure involved the use of benzoyl-*carbonyl*-^{13}C peroxide (^{13}C-BPO) as initiator of polymerizations at 60 °C of MMA or STY containing the STL analogue at a concentration in the region of 10^{-2} times that of the principal monomer. After purification, each polymer was examined by ^{13}C NMR so that it was possible to compare the number of benzoate end groups attached to units derived from the principal monomer with the number joined to units from the additive.[1]

In many respects, MMA has advantages over STY as the reference monomer for study of the reactivities of STL analogues. The chief reason for preferring MMA is because it is less reactive by a factor of 8 than STY toward the $C_6H_5COO^\bullet$ radical. Reaction of the radical with the STL analogue is therefore relatively favored when MMA rather than STY is used as the principal monomer. This advantage is offset by the tendency of MMA to give polymers with higher molecular weights and therefore lower concentrations of end groups; this effect can be overcome by using dilute solutions of the monomer but then decarboxylation of the benzoyloxy radical becomes more pronounced so that many of the end groups are formed from phenyl radicals. The loss of some benzoyloxy radicals in this way does not by itself affect the competition between the principal monomer and the STL analogue for capture of the radicals and formation of benzoate end groups, but there is a reduction in the total number of such groups. Another point favoring MMA instead of STY is the fact that the former contains no aromatic groups; detection by ^{13}C NMR of the incorporation of small amounts of a STL analogue in the body of the polymer may therefore be more reliable.

The first experiments involved the use of a spectrometer operating at 25 MHz for carbon-13, but the instrument was being used at the limit of its capabilities and very long collection times were needed to obtain usable spectra. Subsequently, an opportunity arose to examine some polymers in a spectrometer operating at 100 MHz for carbon-13; the much improved sensitivity and resolution made it possible to use STY as prinicipal monomer without difficulty. The results from the lower field instrument are still regarded as useful if only for screening purposes.

Experimental Section

Many of the experimental procedures have been specified already.[1] The STL analogues were prepared by phase-transfer-catalyzed Wittig reactions, essentially as described for derivatives of STL.[3,5]

According to capillary GC/MS, the samples of Biph-STL and Anth-STL consisted of single isomers, M^+ corresponding to values of m/z of 256 and 280, respectively. The melting points of Biph-STL and Anth-STL were 221–221.5 and 134–135 °C, respectively, in agreement with literature values[7] of 219–220 and 132 °C for the *E* isomers. Capillary GC/MS showed that the sample of Naph-STL contained about 17% of the *Z* isomer; the two isomers had indistinguishable mass spectra and both gave a value of m/z of 230 for M^+. The melting point of the sample of Naph-STL was 60–69 °C; the quoted value[8] for the *E* isomer is 70–70.5 °C. The sample of Phen-STL contained 70% of the *E* isomer; the mass spectra of the two isomers could not be separated and M^+ gave m/z as 280. The melting point of the product was 91–102 °C; the reported value[9] for the *E* isomer is 118 °C. For the purposes of the present work, it was regarded as unnecessary to apply the method involving iodine to convert the samples of Naph-STL and Phen-STL to the pure *E* isomers.

Polymerizations were performed at 60 °C with toluene as diluent in the absence of air; the concentrations of the principal monomer and BPO were in the regions of 2.0 and 1×10^{-2} mol L^{-1}, respectively, and the values of [STL analogue]/[principal monomer] were in the range 0.50×10^{-2} to 3.50×10^{-2}. The reactions were monitored by dilatometry and conversions did not exceed 10%. Polymers were recovered by precipitation in methanol and purified by reprecipitation, usually from solutions in toluene, but certain samples of polyMMA were precipitated from solution in ethyl acetate.

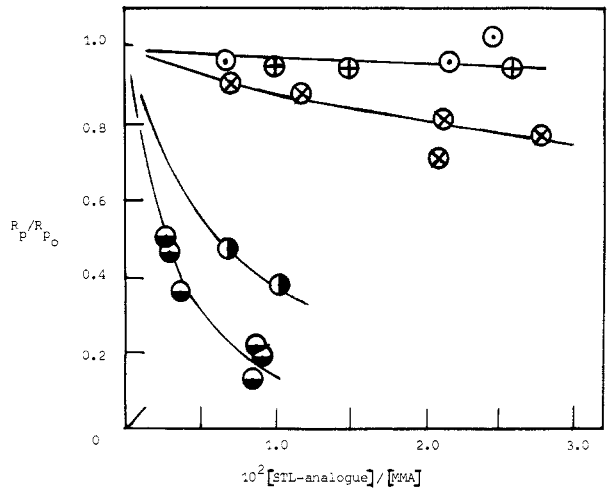


Figure 1. Effects of arylstyrenes upon the rate of polymerization of MMA for fixed concentrations of monomer and BPO. R_{p_0} = rate without additive; R_p = rate in the presence of Biph-STL (⊙), Naph-STL (⊕), Phen-STL (⊗), and Anth-STL (◒). Similar experiments involving AIBN and Anth-STL (◑).

The 100-MHz ^{13}C NMR spectra were recorded on a BRUKER WH400 instrument using a 10-mm probe and the 25-MHz spectra on a JEOL FX 100 spectrometer, as described previously,[1] using 10% w/v solutions in $CDCl_3$.

Results

Figure 1 shows that Biph-STL and Naph-STL had very little effect on the rate of polymerization of MMA initiated by BPO, that Phen-STL caused noticeable retardation, and that Anth-STL produced quite marked reduction in the rate. When AIBN was used as initiator, retardation was evident only for Anth-STL and it was less pronounced than in the experiments involving BPO.

Parts of the 100-MHz ^{13}C NMR spectra of samples of polySTY prepared by using ^{13}C-BPO as initiator are shown in Figure 2; the signals originated from the carbonyl carbons in benzoate groups derived from the peroxide. Spectrum I refers to a polymer prepared in the absence of any STL analogue; it resembles that published by Moad et al.[10] for a low-conversion polymer. The main peak at δ ca. 166.2 is associated with end groups $C_6H_5COOCH_2CH(C_6H_5)$– produced by tail addition and the smaller upfield signals correspond to end groups $C_6H_5COOCH(C_6H_5)CH_2$–, some arising from head addition and others from primary radical termination and transfer to initiator.[10] In spectrum I, the ratio of the areas covered by the upfield and downfield signals is 0.16:1. When using 25-MHz spectra, it was not possible to distinguish with certainty between the two types of benzoate end groups in polySTY.

Spectra II, III, and IV in Figure 2 refer to polymers prepared in the presence of Biph-STL, Naph-STL, and Phen-STL, respectively. As in spectrum I, the prominent downfield signals are attributed to benzoate end groups formed by tail addition of the benzoyloxy radical to STY. The upfield signals are more pronounced than in spectrum I and somewhat different in form; it must be supposed that they include contributions from $C_6H_5COOCH(C_6H_5)CH_2$– groups and also from benzoate groups which are neighbors to units derived from the STL analogue. In each case, let a' represent the area covered by the signal near δ 166 and

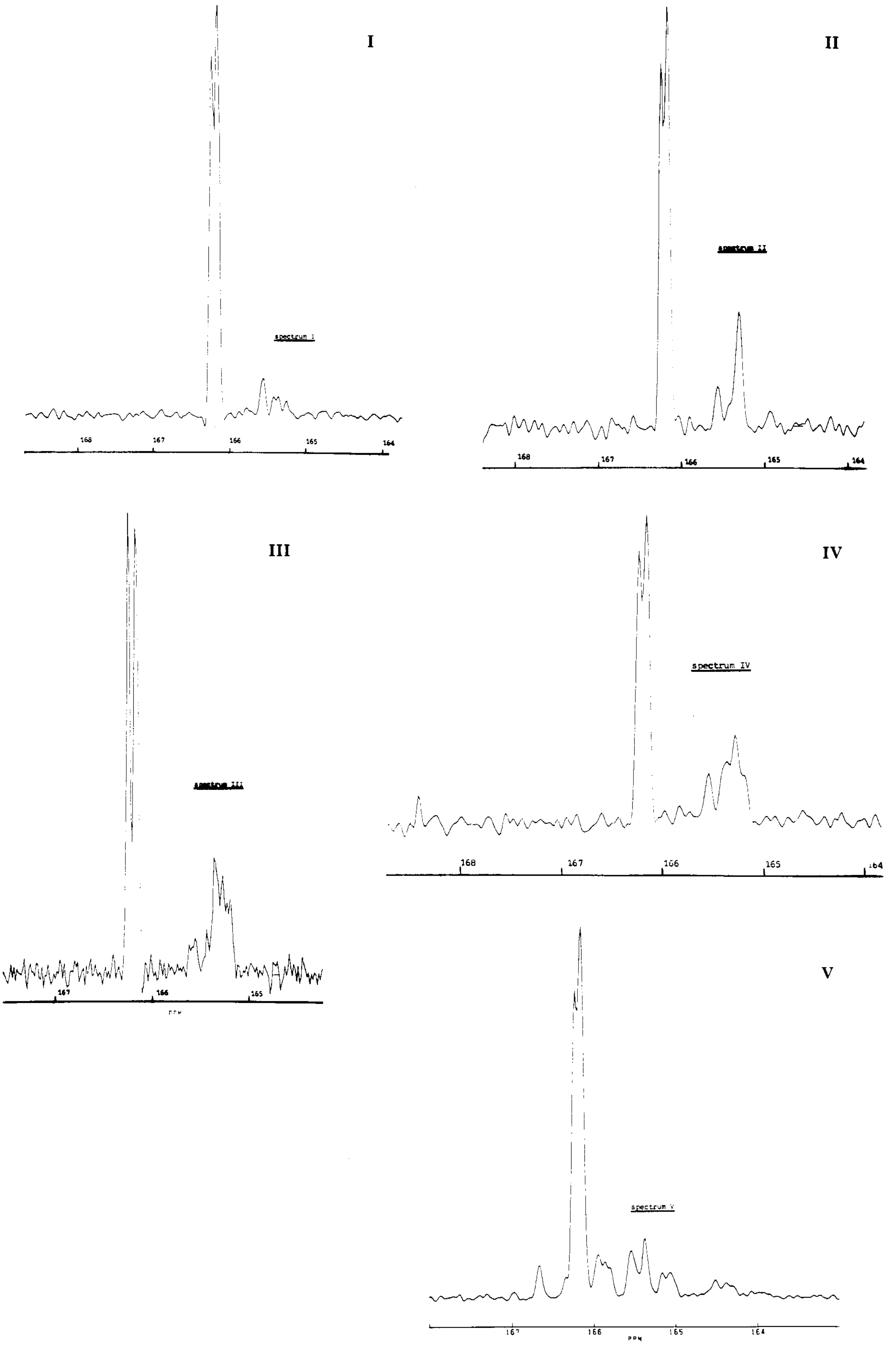


Figure 2. Parts of the 100-MHz ^{13}C NMR spectra of polymers of STY prepared by using ^{13}C-BPO. Polymer prepared without arylstyrenes (I). Polymer prepared from system containing Biph-STL (II), Naph-STL (III), Phen-STL (IV), and Anth-STL (V). Values of [additive]/[STY] given in text.

a'' that corresponding to the remaining signals; the values of a''/a' for spectra II, III, and IV are 0.34, 0.50, and 0.55, respectively. In principle, it is possible to use information derived from spectrum I to modify a''/a' to give

$A''/A' = r =$

(area for peaks corresponding to C_6H_5COO– attached to STL analogue)/(area for peaks corresponding to C_6H_5COO– attached to STY by an initiation process)

A'' must be less than a'' because the latter includes a contribution from benzoate groups attached to the heads of STY units; also A' must be greater than a' because some of the $C_6H_5COOCH(C_6H_5)CH_2$– groups are formed during initiation. The conversion of a'' to A'' is easily made by using the results from spectrum I, which showed that, in the absence of an analogue of STL, a''/a' is 0.16. It is less easy to evaluate the difference between a' and A' because of uncertainty concerning the relative importances of head initiation, primary radical termination and transfer to initiator in the formation of $C_6H_5COOCH(C_6H_5)CH_2$– groups; it is assumed that 75% of these end groups result from initiation. The values of A''/A' for spectra II, III, and IV are therefore taken as $(0.34 - 0.16)/(1 + 0.12)$, $(0.50 - 0.16)/(1 + 0.12)$, and $(0.55 - 0.16)/(1 + 0.12)$, i.e., 0.16, 0.30, and 0.35, respectively. Each value of r is also given by k[STL analogue]/k_s[STY] where the concentrations refer to the reaction mixture from which the polymer was made and k and k_s are respectively the velocity constants for the attachments of the benzoyloxy radical to the STL analogue and to STY, respectively. Therefore, k/k_s is given by r[STY]/[STL analogue]. In the reaction mixtures which yielded the polymers corresponding to spectra II, III, and IV, [Biph-STL]/[STY], [Naph-STL]/[STY], and [Phen-STL]/[STY] were 1.22×10^{-1}, 2.25×10^{-2}, and 2.30×10^{-2} respectively; the corresponding values of k/k_s are therefore 13, 13, and 15.

Spectrum V in Figure 2 refers to polySTY prepared in the presence of Anth-STL; it is rather more complex than spectra II, III, and IV. There is an additional peak downfield from that due to $C_6H_5COOCH_2CH(C_6H_5)$–. In this case, a'' is taken as the total area covered by peaks other than that near δ 166; a''/a' is 0.56 so that r, as defined above, becomes $(0.56 - 0.16)/1.12$, i.e., 0.36. In the feed, [Anth-STL]/[STY] was 0.55×10^{-2} so that k/k_s is 65.

The published result[1] for the relative reactivities of STL and STY toward the benzoyloxy radical should be modified because of the contribution of $C_6H_5COOCH(C_6H_5)CH_2$– end groups to the NMR peaks previously attributed entirely to benzoate groups attached to STL units. The sample of polySTY was prepared from a system in which [STL]/[STY] was 0.748 and the value of a''/a' (in a 25-MHz spectrum) was 5.5; according to the procedure developed here, A''/A' is $(5.5 - 0.16)/1.12$, i.e., 4.8, so that the revised value of k/k_s is 6.4.

Parts of the 100-MHz ^{13}C NMR spectra of samples of polyMMA prepared by using ^{13}C-BPO are displayed in Figure 3. Spectrum VI refers to the polymer from a system not containing a STL analogue. The peaks near δ 166 arise from the enriched carbonyl carbon atoms in benzoate groups attached to the tails of MMA units. There are no subsidiary signals which could be associated with benzoate groups joined to the heads of monomeric units; in this respect, MMA can be regarded as more satisfactory than STY as a reference monomer. Spectrum VII corresponds to the polymer from a system in which [Biph-STL]/[MMA] was 1.06×10^{-2}; the peaks near δ 166 resemble those in spectrum VI but they are accompanied by a prominent structured signal at δ ca. 165.5. This upfield signal is attributed to benzoate end groups attached to Biph-STL units. This assignment is made on the basis of 25-MHz ^{13}C NMR spectra (see examples in Figure 4) for polymers of MMA prepared in the presence of STL analogues; the upfield signals grow relative to the downfield signals with increase of [STL analogue]/[MMA] in the feed. Following the procedure already described but noting that no correction is needed to find A''/A' for spectrum VII, that quantity is found to be 0.92, leading to a value of 87 for k/k_m for Biph-STL. From the information provided with Figure 4, the values of k/k_m for Naph-STL are found to be 92 and 98 from spectra IX and X, respectively; the agreement between the two results is surprisingly good in view of the uncertainties in the integrations of the spectra.

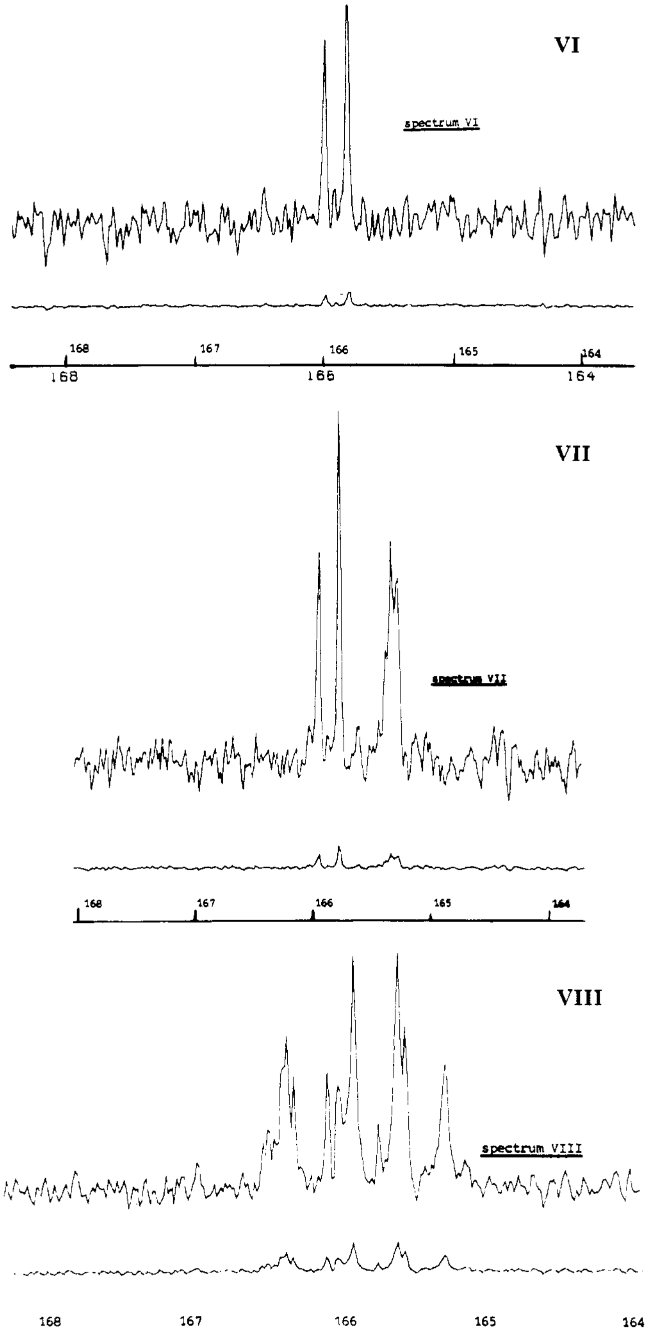


Figure 3. Parts of the 100-MHz ^{13}C NMR spectra of polymers of MMA prepared by using ^{13}C-BPO. Polymer prepared without arylstyrene (VI). Polymer prepared from system containing Biph-STL (VII) and Anth-STL (VIII). Values of [additive]/[MMA] given in text.

Spectrum VIII (Figure 3) refers to polyMMA from a system in which [Anth-STL]/[MMA] was 0.975×10^{-2}; as

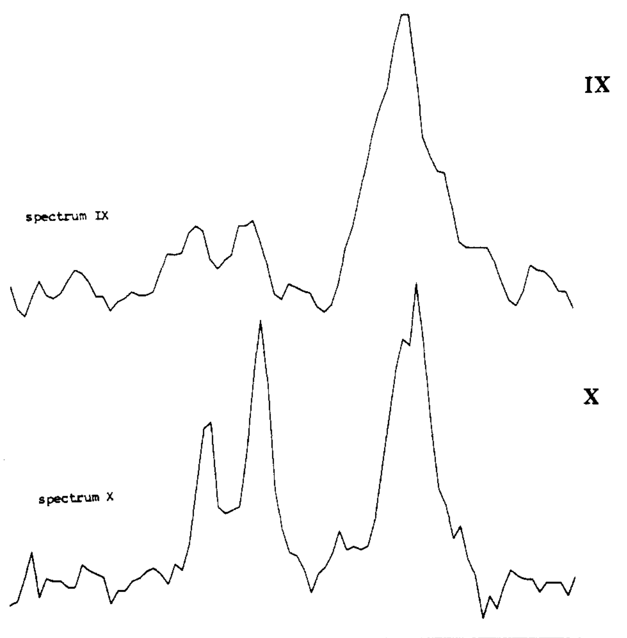


Figure 4. Parts of the 25-MHz ^{13}C NMR spectra of polymers of MMA prepared by using ^{13}C-BPO and Naph-STL. $10^2 \times$ [Naph-STL]/[MMA] –1.30 (IX), 3.41 (X); (area for upfield signals)/(area for downfield signals) –1.20 (IX), 3.33 (X).

for the corresponding polymer of STY (spectrum V in Figure 2), the spectrum is rather complex. At this stage, it is not possible to separate the peaks associated with benzoate groups attached to MMA and those due to initiator fragments adjacent to Anth-STL units; there is, however, a prominent signal downfield from the position expected for $C_6H_5COOCH_2C(CH_3)(COOCH_3)$– and also other signals well upfield from that position.

Polymerizations of MMA were performed by using ^{13}C-AIBN as initiator with various STL analogues as additives. The 25-MHz ^{13}C NMR spectra of the polymers gave no indication of the presence of $(CH_3)_2C(CN)$– groups attached to units derived from the STL analogues. The value of [Anth-STL]/[MMA] in one of these experiments was 3.40×10^{-2}, i.e., more than three times that for the polymerization corresponding to spectrum VIII (Figure 3), which contains prominent signals that can only be associated with benzoate groups joined to units derived from Anth-STL; the signals due to benzoate groups adjacent to Anth-STL units were also very evident in 25-MHz spectra although the signals were not well resolved. Evidently the STL analogues resemble the parent compound[1] in having very low reactivity toward the 1-cyano-1-methylethyl radical.

In the cases of STL and its *p*-fluoro derivative, ^{14}C labeling was used for measurement of the total incorporation of the additive by copolymerization with STY, MMA, and other monomers.[2] Similar work has not been performed with the STL analogues considered here but the 100-MHz ^{13}C NMR spectra of samples of polyMMA have been examined for evidence of the presence of aromatic units in the polymers; the polymers had been purified by two reprecipitations from ethyl acetate to eliminate the possibility of occlusion of aromatic solvent. For a polymer prepared in the presence of Anth-STL, small but clear signals were found in the range δ 120–140; they were larger than would have been expected if the additive had been incorporated only at sites adjacent to the benzoate end groups, suggesting that there was slight but appreciable inclusion of Anth-STL in the body of the polymer. Previous results[2] suggest that the incorporation of STL analogues would be rather more pronounced for polymerizations involving monomers not possessing α-methyl groups.

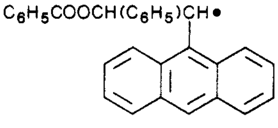
Discussion

Consideration of the reactions of the benzoyloxy radical with the analogues of STL will be based on the view that generally the products can be represented as $C_6H_5COOCH(C_6H_5)CHAr$; as will be pointed out, the case of Anth-STL is probably somewhat different. The evidence for the high reactivity of STL toward the benzoyloxy radical is not based solely upon the results of the work with ^{13}C-BPO. Similar conclusions were reached from studies of the effects of STL on the decomposition of BPO in dilute solution in benzene;[11] it caused a marked decrease in the yield of carbon dioxide, resulting from decarboxylation of the benzoyloxy radical, without affecting the rate of dissociation of the peroxide or the yield of benzoic acid. It was also shown directly[12] that the presence of STL during the polymerization of STY or MMA initiated by BPO increased the ratio of benzoate to phenyl end groups without affecting the total rate of incorporation of initiator fragments.

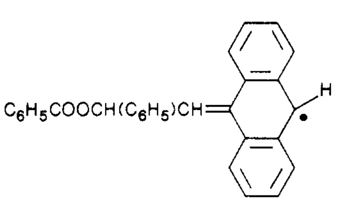
For assessment of the reactivities of unsaturated compounds toward the 1-cyano-1-methylethyl radical, only the procedure involving ^{13}C initiator is applicable. The inertness of STL and related compounds toward this radical was confirmed for Anth-STL and other analogues, the presence of which in the polymerizing systems had no detectable effect on the NMR signals arising from $(^{13}CH_3)_2C(CN)$– end groups in the resulting polymers. Confirmation of the great difference between the reactivities of $C_6H_5COO^\bullet$ and $(CH_3)_2C(CN)^\bullet$ toward STL and related compounds has been provided by the results of experiments of a different type, involving 4-fluorostilbene (F-STL).[13] The F NMR spectrum of polySTY prepared in the presence of F-STL, with AIBN as initiator, contained peaks attributable to the few in-chain F-STL units. Identical signals were found in the spectrum of polySTY prepared similarly but with BPO as initiator; there were, however, additional well-separated strong signals which could only have been due to F-STL units in a very different environment, viz., adjacent to benzoate end groups.

Spectra II, III, and IV and previous results show that the resonances due to the carbonyl carbon atoms in benzoate groups adjacent to units derived from STL, Biph-STL, Naph-STL, and Phen-STL are similar and occur at δ ca. 165.5, i.e., upfield from the corresponding signal for $C_6H_5COOCH_2CH(C_6H_5)$–, but overlapping those for the end groups $C_6H_5COOCH(C_6H_5)CH_2$–. The view that the polymers prepared in the presence of these additives contain end groups $C_6H_5COOCH(C_6H_5)CHAr$– is therefore entirely reasonable. The ^{13}C NMR signals from benzoate end groups in polySTY or polyMMA prepared in the presence of Anth-STL are rather complex; for both polymers, there is quite a prominent component about 1 ppm *downfield* from the signal due to the initiator fragment joined to the principal monomeric unit. Clearly the reaction between the benzoyloxy radical and Anth-STL can proceed in more than one way, leading to several products which will become incorporated in polymer. The most likely possibilities are shown as radicals I, II, and III.

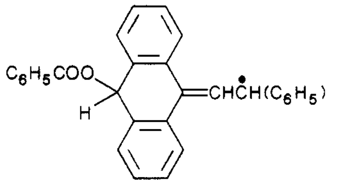
If these radicals grow by addition of MMA or STY or if they engage in a process resembling primary radical termination by combination, they form end groups. It is probable that the NMR signal from the enriched carbonyl site in an end group corresponding to I would be similar to those found when the benzoate group is linked to the head of a STY unit or to a unit derived from STL; the end groups corresponding to radicals II and particularly III



I



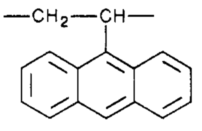
II



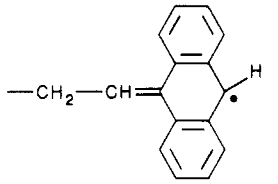
III

might give signals which are shifted quite appreciably, the latter perhaps being sensitive to ring-current influences.

It is relevant that radical polymerizations of 9-vinylanthracene lead to units of two types, IV and V, corresponding to structures I and II; the polymerizations are slow and lead to polymers having quite low molecular weights. Structure IV results from the opening of the ethylenic bond leaving the anthryl group pendant; addition across the ring to give structure V is dominant.[14] Structures analogous to II and III can be written for the products from the reactions of the benzoyloxy radical with STL, Biph-STL, Naph-STL, and Phen-STL; according to the ^{13}C NMR spectra, they are not present in the polymers to a detectable extent as expected for energetic reasons.



IV



V

Marked retardation of the polymerization of MMA was caused by Anth-STL. It can be explained by supposing that some of the products of the interaction of $C_6H_5COO^\bullet$ with Anth-STL react sluggishly with monomeric MMA and engage in an alternative process resembling primary radical termination. Another process also must be operating since the polymerization was retarded by Anth-STL even when AIBN was used as initiator and there is no evidence for direct reaction of the 1-cyano-1-methylethyl radical with Anth-STL. It must be concluded that the occasional incorporation of Anth-STL in the growing polymer chain can lead to a product radical of comparatively low reactivity. As pointed out already, there is spectral evidence for slight incorporation of Anth-STL in polyMMA, in excess of that at sites adjacent to benzoate groups. Of the other analogues of STL, only Phen-STL caused detectable retardation and in no case was incorporation indicated by ^{13}C NMR signals in the region δ 120–140. Clearly it would be desirable to examine these systems by using the STL analogues either labeled with carbon-14 or tritium or enriched with carbon-13 so that the total incorporation could be detected, measured, and characterized.

The sample of Phen-STL contained the E and Z isomers in the proportions 70:30. Previous work has shown that for STL[1] and its 4-methoxy-4′-chloro derivative[5] with the benzoyloxy radical, the *E* isomer is the more reactive by a factor of 2 or 3. It is therefore reasonable to increase the velocity constant found for Phen-STL to allow fair comparisons with other analogues of STL for which pure *E* isomers were used. The "effective" concentration of Phen-STL can be related to the actual concentration by supposing that 70% of the substance exhibits the "full" reactivity of the *E* isomer while the remainder has a reactivity lower by a factor of 2.5; the ratio of "effective" to actual concentration is taken as [0.70 + (0.30/2.5)]:1 i.e., 0.82:1. The observed value of 15 for k/k_s for Phen-STL becomes 15/0.82, i.e., 18. A correction of the same type is applied in the case of Naph-STL; the ratio of the "effective" and actual concentrations is (0.83 + (0.17/2.5)]:1, i.e., 0.90, so that the observed value of k/k_s is increased from 13 to 14. The values of k/k_s for the *E* isomers of STL, Biph-STL, Naph-STL, Phen-STL, and Anth-STL are therefore taken as 6, 13, 14, 18, and 65, respectively.

The experiments with MMA as reference monomer led to a value of 87 for k/k_m for Biph-STL, to be compared with 104 expected on the basis of k/k_s and k_s/k_m[15] being 13 and 8, respectively; the agreement is not good, probably because of difficulties associated with the analysis of the NMR spectra. A similar comparison can be made between the results for Naph-STL using STY and MMA as reference monomers. The 25-MHz spectra IX and X led to values of 92 and 97 for k/k_m modified to 102 and 108 by the procedure already described to allow for the presence of the *Z* isomer in the sample of Naph-STL; taking k_s/k_m as 8, the calculated values of k/k_s are then 13 and 14, in good agreement with that obtained when using STY as reference monomer.

The differences between the reactivities of STL and its analogues can be explained qualitatively in terms of the resonance stabilization of the radicals $C_6H_5COOCH(C_6H_5)CHAr^\bullet$. In this connection it should be noted that the relative reactivities of STY, 4-vinylbiphenyl (VBP), and 2-vinylnaphthalene (VN)[16] toward the benzoyloxy radical (1, 3.5, and 2, respectively) can be explained similarly. The monomers VPB and VN, unlike Biph-STL and Naph-STL, also display high reactivity toward the $(CH_3)_2C(CN)^\bullet$ radical because tail addition of the radical is not sterically impeded.

The case of acenaphthylene, another 1,2-disubstituted monomer, is quite different; it readily undergoes radical homopolymerization and copolymerization[17] and shows high reactivity to both the benzoyloxy and 1-cyano-1-methylethyl radicals.[18] These features can be associated with strain in the five-membered ring of the monomer and its partial relief by opening of the olefinic double bond.

For unsaturated substances including those that do not readily undergo radical homopolymerization, reactivity toward the benzoyloxy radical can be assessed by a procedure involving comparison of the numbers of benzoate and phenyl end groups in a copolymer prepared from a mixture of a monomer, say MMA, with the unsaturated substance under examination with BPO as initiator;[19] use can be made of peroxide doubly labeled with carbon-14 and tritium. The procedure properly applied leads to accuracy and sensitivity appreciably greater than possible by the use of ^{13}C-BPO followed by examination of benzoate end groups by NMR spectroscopy; it lacks specificity, however, in the sense that it does not reveal that a benzoate end group can be attached in more than one way to a unit derived from Anth-STL, just as it cannot distinguish between the end groups apparently resulting from tail and head additions of the benzoyloxy radical to STY.

It should be noted that spectrum VI (Figure 3) provides no evidence for the attachment of benzoate end groups to the heads of MMA units; it is possible of course that there is overlap of the signals corresponding to the two types of benzoate end groups. Differences between the cases of

STY and MMA, with respect to head addition of the benzoyloxy radical, can be regarded as another consequence of the steric hindrance caused by the double substitution at the carbon atom at the head of the molecule of MMA. Solomon and co-workers,[20,21] using a procedure involving a radical scavenger, concluded that tail addition of the benzoyloxy radical to MMA at 60 °C occurs about 13 times as frequently as head addition. An earlier report,[22] that head addition is dominant, was shown to be in error and the conclusion[23] was reached that there is almost exclusively tail addition of $C_6H_5COO^\bullet$ to MMA.

It is still not clear why STL and related compounds are so effective in capturing benzoyloxy radicals. It appears that the presence of an aromatic grouping attached directly to each of the carbon atoms of the ethylenic bond is necessary for high reactivity toward the radical; thus 1,3-diphenylpropene (DPP) has a reactivity considerably less than that of STL but comparable to that of STY.[19] Similarity between DPP and STY is expected since the radicals $C_6H_5COOCH(CH_2C_6H_5)CH(C_6H_5)^\bullet$ and $C_6H_5COOCH_2CH(C_6H_5)^\bullet$ are most probably stabilized to about the same extent. Attachment of the benzoyloxy radical to STY can occur at either end of the ethylenic bond although formation of $C_6H_5COOCH_2CH(C_6H_5)^\bullet$ is greatly preferred.[10] On the other hand, the two ends of the double bond in STL must be equally reactive; on that basis, the reactivity of STL toward $C_6H_5COO^\bullet$ could be expected to be twice that of STY whereas it is found that the reactivities differ by a factor of about 6.

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Registry No. (*E*)-Biph-STL, 2039-69-2; (*E*)-Anth-STL, 42196-97-4; Naph-STL, 2043-00-7; Phen-STL, 1895-98-3; BPO, 94-36-0; (MMA)(BPO) (copolymer), 80-62-6; STY, 100-42-5.

References and Notes

(1) Bevington, J. C.; Huckerby, T. N. *Macromolecules* **1985**, *18*, 176–178.
(2) Barson, C. A.; Bevington, J. C. *Eur. Polym. J.* **1987**, *23*, 251–253.
(3) Bevington, J. C.; Breuer, S. W.; Huckerby, T. N. *Angew. Makromol. Chem.* **1986**, *140*, 145–152.
(4) Weale, K. E. *Polymer* **1987**, *28*, 2151–2156.
(5) Bevington, J. C.; Breuer, S. W.; Huckerby, T. N. *Polym. Bull. (Berlin)* **1984**, *12*, 531–534.
(6) Bevington, J. C.; Huckerby, T. N.; Liu, M. G.; Thorpe, F. G. *Eur. Polym. J.* **1987**, *23*, 95–97.
(7) Drefahl, G.; Ponsold, K. *Chem. Ber.* **1960**, *93*, 472–481.
(8) Everett, J. L.; Kon, G. A. R. *J. Chem. Soc.* **1948**, 1601–1603.
(9) Bergmann, E. D.; Bergmann, F. *J. Am. Chem. Soc.* **1937**, *59*, 1443–1450.
(10) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982**, *15*, 1188–1192.
(11) Bevington, J. C.; Brooks, C. S. *Makromol. Chem.* **1958**, *28*, 173–175.
(12) Bevington, J. C.; Johnson, M. *Makromol. Chem.* **1967**, *102*, 73–82.
(13) Bevington, J. C.; Huckerby, T. N.; Vickerstaff, N.; Barson, C. A. *Polymer* **1986**, *27*, 1823–1825.
(14) Rembaum, A.; Eisenberg, A. *Macromol. Rev.* **1967**, *1*, 57–90.
(15) Bevington, J. C.; Ebdon, J. R. In *Developments in Polymerisation—2*; Haward, R. N., Ed.; Applied Science: London, 1979; Chapter 1.
(16) Bevington, J. C.; Ayrey, G. *Eur. Polym. J.* **1987**, *23*, 497–499.
(17) Ballesteros, J.; Howard, G. J.; Teasdale, L. *J. Macromol. Sci., Chem.* **1977**, *A11*, 29–37.
(18) Ayrey, G.; Bevington, J. C. *J. Macromol. Sci., Chem.* **1985**, *A22*, 229–234.
(19) Barson, C. A.; Bevington, J. C.; Breuer, S. W.; Huckerby, T. N., to be submitted for publication.
(20) Cuthbertson, M. J.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Polym. Bull. (Berlin)* **1982**, *6*, 647–651.
(21) Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 1573–1588.
(22) Kamachi, M.; Kuwae, Y.; Nozakura, S. *Polym. Bull. (Berlin)* **1981**, *6*, 143–146.
(23) Kunitake, T.; Murakami, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 67–81.

Effect of Phase Transition on Photosensitized Radical Polymerization of Diene-Containing Lipids as Liposomes[1]

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ABSTRACT: 1,2-Bis(2,4-octadecadienoyl)-*sn*-glycero-3-phosphorylcholine (DODPC) was polymerized in liposomes by organic free radicals which were generated by photosensitized cleavage of the added azo-type radical initiators such as azobis(isobutyronitrile) (AIBN) or azobis(2-amidinopropane) dihydrochloride (AAPD). Selective polymerization of diene groups on the 1- or 2-acyl chain of DODPC was carried out with water-insoluble AIBN or water-soluble AAPD, respectively, at any temperature, even at temperatures lower than the phase transition temperature (T_c) of the DODPC liposomes. The diene group in the 1-acyl chain locates in the hydrophobic region of the bilayer, whereas that in the 2-acyl chain faces an aqueous phase at any temperature. When AAPD was added to the outer aqueous phase of DODPC liposomes, polymerization conversion initiated by the photosensitized AAPD radicals reached around 50% above the T_c but it remained 27% below the T_c. This confirms that AAPD added to the outer aqueous phase of the liposome can penetrate the lipid membrane above the T_c, but not below it. The liposomes which were polymerized in either the outer or the inner half of the bilayer membrane were therefore prepared by applying this penetration profile. The liposomes polymerized only in the outer layer were as stable as those fully polymerized. The initial polymerization rate of DODPC initiated by photosensitized AIBN radicals in the lipid membrane also reflected the membrane viscosity. Lower polymerization conversions, reflecting considerable recombination of free radicals, were found below T_c due to higher membrane microviscosity.

Introduction

Phospholipid liposomes are being applied as microcapsules for carriers of drugs or functional particles as well as models for biomemranes.[2] These liposomes are, however, not very stable and generally cause aggregation and fusion. Polymerization of monomeric lipids is considered to be a potential technique to stabilize the lipid assemblies.[3,4] The polymerized lipid liposomes actually provide stable microcapsules in some cases, but we have already warned that the membrane stability deeply depends on

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