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The Involvement of Stilbene in Radical Polymerizations of Methyl Methacrylate and Styrene

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ABSTRACT: Polymerizations of methyl methacrylate and styrene, initiated by benzoyl-*carbonyl*-^{13}C peroxide and performed in the presence of *trans*-stilbene, lead to polymers containing appreciable numbers of the end groups $C_6H_5COOCH(C_6H_5)CH(C_6H_5)$– detected by NMR spectroscopy; very little stilbene is incorporated in the polymer chains. When the polymerizations are initiated by sources of the radical $(^{13}CH_3)_2C(CN)\cdot$, there is negligible reaction of the primary radicals with stilbene. The results show that stilbene is very reactive toward the oxygen-centered benzoyloxy radical but very unreactive toward the carbon-centered 2-cyano-2-propyl, poly(methyl methacrylate), and polystyrene radicals.

This paper is concerned mainly with the effects of *trans*-stilbene (STL) upon initiation processes in the radical polymerizations of methyl methacrylate (MMA) and styrene (STY) using benzoyl peroxide (BPO), azoisobutyronitrile (AIBN), and 2-cyano-2-propylazoformamide (AZOF). It provides another example of the applications of NMR spectroscopy to studies of end groups and the value of the procedure for the understanding of the reactions occurring in polymerizing systems.

The rate of decomposition of BPO in benzene at 60 °C is unaffected by the presence of STL at concentrations up to at least 50 g/L but there are marked reductions in the yield of carbon dioxide formed by decarboxylation of benzoyloxy radicals.[1] The presence of STL causes only slight increases in the amount of benzoic acid produced in the systems and so the effects on the production of carbon dioxide can be explained by ascribing to the additive high reactivity for capture of $C_6H_5COO\cdot$ radicals. This conclusion has been confirmed by results of experiments in which BPO was used to initiate polymerizations of STY and MMA in the presence of STL.[2] The rate of polymerization was not affected by the presence of the additive but the balance between benzoate and phenyl end groups in the polymers was shifted, in the sense that the proportion of the ester end groups was increased. it appeared that the polymers contained comparatively high proportions of the end groups $C_6H_5COOCH(C_6H_5)CH(C_6H_5)$–.

The results indicate that the reactivities at 60 °C of STY, MMA, and STL for capturing the benzoyloxy radical are in the proportions 1.0:0.12:4.8. The high reactivity of STL toward the radical $C_6H_5COO\cdot$ can be contrasted with its low reactivity toward polymer radicals of various types as shown by its failure to copolymerize with STY[3] or MMA.[2]

To study further the reactions of STL with primary radicals, use has been made of a new procedure for examination of the reactivities of unsaturated substances.[4] Radicals enriched with carbon-13 are generated in a mixture of monomers. From the NMR spectrum of the resulting copolymer, it is possible in suitable cases to compare the numbers of primary radicals attached to the two types of monomer unit and then to find the relative values of the velocity constants for the reactions of the radical with the two monomers. In the present work, benzoyl-*carbonyl*-^{13}C peroxide (^{13}C-BPO) has been used as a source of $C_6H_5{}^{13}COO\cdot$ radicals at 60 °C; $(^{13}CH_3)_2C(CN)\cdot$ radicals have been generated from suitably enriched AIBN at 60 °C or AZOF at 100 °C.

Experimental Section

Details have already been given of preparations and purifications of materials and of procedures for recording ^{13}C NMR spectra using a JEOL FX100 Fourier-transform spectrometer operating at 25.05 MHZ.[2,4,5] Polymerizations were performed with toluene as diluent in sealed tubes in the absence of air; conversions did not exceed 10%. Polymers were recovered by precipitation in methanol, purified by reprecipitation, and dried in vacuum at 50 °C; tests showed that complete removal of unreacted initiator and monomers was achieved.

Results and Discussion

Polymers of MMA were prepared at 60 °C by using monomer at about 2 mol/L, ^{13}C-BPO at about 2 g/L, and various concentrations of STL so that the values of

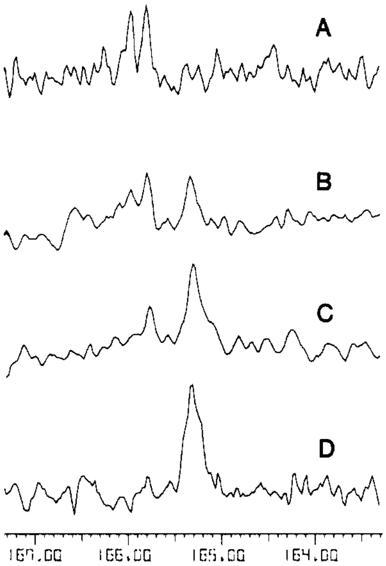

Figure 1. Parts of the ^{13}C NMR spectra of polymers of methyl methacrylate prepared at 60 °C from solutions of the monomer with *trans*-stilbene in toluene; polymerizations initiated with benzoyl peroxide enriched in the carbonyl groups with carbon-13. Initial values of [stilbene]/[methyl methacrylate] are 0, 0.021, 0.046, and 0.969 for A, B, C, and D, respectively.

[STL]/[MMA] were 0, 0.021, 0.046, and 0.969 (experiments A, B, C, and D, respectively). Figure 1 refers to the ^{13}C NMR spectra of these polymers. Polymer A gives a spectrum with peaks at δ 165.8 and 165.5 attributed to benzoate end groups in the homopolymer of MMA. With increasing concentration of STL in the reaction mixture, a new peak at δ 165.3 grows; the peaks around δ 165.7 diminish and cannot be detected for polymer D. The results can be interpreted in terms of competing initiation processes involving the benzoyloxy radical

$$C_6H_5COO\cdot + MMA \rightarrow C_6H_5COO(MMA)\cdot$$

$$\text{velocity constant} = k_m$$

$$C_6H_5COO\cdot + STL \rightarrow C_6H_5COO(STL)\cdot$$

$$\text{velocity constant} = k_s$$

The initiator fragment attached to a STL unit is responsible for the NMR signal at δ 165.3 (see later). The relative numbers of the two types of benzoate end groups can be found by comparison of the areas under the appropriate peaks in the spectra.[4] Use of the relationship

$$\frac{\text{no. of } C_6H_5COO(MMA)\text{– end groups}}{\text{no. of } C_6H_5COO(STL)\text{– end groups}} = \frac{k_m[MMA]}{k_s[STL]} \quad (1)$$

leads to values of k_m/k_s of 0.024 and 0.025 from measurements on polymers B and C, respectively, confirming the high reactivity of STL toward the primary radical and agreeing well with the results of previous experiments involving ^{14}C-BPO.[2]

If STL units were present in the polymers to an appreciable extent, they would be expected to give their own signals in the region δ 120–140; such signals could not be recognized in any of the spectra. It is estimated that, even for polymer D derived from the reaction mixture richest in STL, there is less than 1 STL unit for 40 MMA units in the polymer. It must be concluded that almost the only STL units incorporated in the polymers are those adjacent to C_6H_5COO–end groups. The end-group signals are quite weak because the concentrations of MMA and STL in the reaction mixtures were comparatively low so that there was appreciable initiation by $C_6H_5\cdot$ radicals produced by decarboxylation of $C_6H_5COO\cdot$ radicals. The present results do not allow comparisons to be made between the reactivities of MMA and STL toward the $C_6H_5\cdot$ radical.

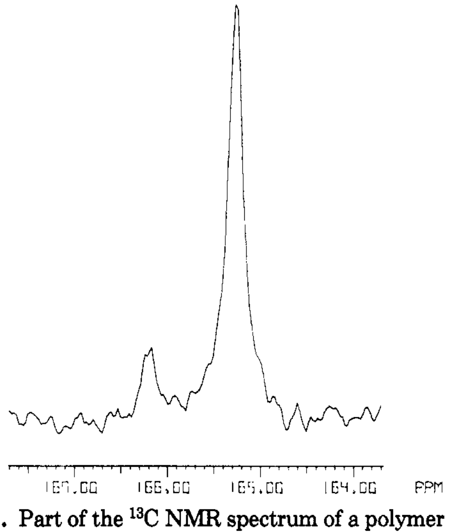

Figure 2. Part of the ^{13}C NMR spectrum of a polymer of styrene prepared at 60 °C from a solution of the monomer with *trans*-stilbene in toluene, [stilbene]/[styrene] = 0.748. Polymerization initiated with benzoyl peroxide enriched in the carbonyl groups with carbon-13.

Figure 2 shows part of the ^{13}C NMR spectrum of a polymer prepared at 60 °C using ^{13}C-BPO as initiator in a system containing STY at 1.07 mol/L and STL at 0.80 mol/L. Consideration of the spectrum of polymer produced correspondingly from STY without added STL indicates that the smaller peak at δ 166.2 in Figure 2 can be ascribed to a $C_6H_5{}^{13}COO$– group attached to the methylene group of a STY unit, i.e., to a structure produced by the normal initiation process in the polymerization of that monomer. The larger peak at δ 165.25 is assigned to the benzoate group attached to a STL unit; this assignment can be justified on the basis of work by Moad et al.[6] They considered the carbonyl resonances for the ethyl, 1-phenylethyl, and 2-phenylethyl esters of benzoic acid. A change of only 0.2 ppm in the carbonyl resonance of ethyl benzoate resulted from introduction of a phenyl group at the β-position; substitution at the α-position, however, caused the carbonyl resonance to shift significantly upfield, the δ value being reduced by about 0.8 ppm. Moad et al.[6] assigned the major downfield resonances for poly(STY) prepared by using ^{13}C-BPO to the grouping $C_6H_5COOCH_2CH(C_6H_5)$– and resonances 0.7–1.0 ppm upfield to chain ends $C_6H_5COOCH(C_6H_5)CH_2$– produced either by "abnormal" initiation or by primary radical termination. The rather small effect due to the β-phenyl group in the model compounds suggests that there can only be a small difference between the carbonyl resonances for the groupings $C_6H_5COOCH(C_6H_5)CH(C_5H_5)$– considered here and $C_6H_5COOCH(C_6H_5)CH_2$– considered by the Australian workers.

The resolution in the spectrum shown in Figure 2 is not good but the areas under the peaks are in the approximate ratio 1:5.5. Application of an equation similar to (1) indicates that STL is about 7 times as reactive as STY toward the benzoyloxy radical; previous results led to a factor of about 5.[2] As in the case of MMA, it is clear that only a very small amount of STL is incorporated in the polymer as a whole and that almost all of it occupies sites adjacent to benzoate end groups. The conclusion about the high reactivity of STL toward $C_6H_5COO\cdot$ is unaffected by the possibility that some of the $C_6H_5COO(STL)\cdot$ radicals entered polymer as a result of a termination process rather than reaction with monomeric MMA or STY.

There are significant differences between the chemical shifts for the signals due to benzoate end groups in homopolymers of STY and MMA prepared by using ^{13}C-BPO; in copolymers of these monomers, however, the ester end groups give a single unresolved peak at the intermediate position of δ 166.1.[7] It is not possible therefore to apply the procedure involving NMR examination of end groups for comparison of the reactivities of MMA and STY toward the benzoyloxy radical; this failure can be contrasted with the success achieved with the MMA/STL and STY/STL systems but it can be explained.

For the MMA/STY copolymers, the signals due to the C_6H_5COO(STY)– and C_6H_5COO(MMA)– end groups must be influenced by the distribution of the two types of monomer unit in the attached macromolecular chains and also by steric relationships between the monomer units. In the systems involving STL, the situation is much simpler; in the case of MMA/STL, for example, both C_6H_5COO(STL)– and C_6H_5COO(MMA)– end groups are attached to long sequences of MMA units so that the effects of the units attached directly to the initiator fragment have a dominant effect upon the carbonyl resonances. It should be noted that the NMR spectra referred to here were recorded on a spectrometer operating at 25.05 MHz. Use of a spectrometer operating at higher field has shown that the peak at δ 166.1 for benzoate end groups in the copolymers of MMA and STY consists of several components and that it may be possible to deduce a great deal of information about the relative numbers of the various possible sequences of monomer units in the chains attached to the benzoate end groups.[8]

Polymerizations of MMA in the presence of STL have also been initiated at 60 °C with ^{13}C-AIBN and at 100 °C with ^{13}C-AZOF so that the $(^{13}CH_3)_2C(CN)$– end groups could be studied by NMR spectroscopy. The presence of STL in the systems, even at a concentration sufficient to make [STL]/[MMA] equal to 1.5, has no effect upon the NMR spectra of the polymers. It is evident that STL is not incorporated to any appreciable extent either in the polymer molecule as a whole or at sites adjacent to 2-cyano-2-propyl end groups. It must be concluded that STL is very unreactive toward the $(CH_3)_2C(CN)\cdot$ radical, although it has such high reactivity toward the $C_6H_5COO\cdot$ radical.

The results of studies with other monomers, including acenaphthylene,[7] suggest that high reactivity toward the benzoyloxy radical coincides with comparatively high reactivity toward the 2-cyano-2-propyl radical. In this respect, *trans*-STL is clearly abnormal. Its low reactivity toward carbon-centered radicals, polystyrene and poly(methyl methacrylate) as well as 2-cyano-2-propyl, may result from steric effects which do not operate for an oxygen-centered radical such as benzoyloxy. It will be necessary to test this hypothesis using radicals of other types.

Registry No. STL, 103-30-0; MMA, 80-62-6; STY, 100-42-5; AIBN, 78-67-1; AZOF, 10288-28-5; BPO, 94-36-0.

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Solid-State NMR Investigation of the Contribution of Anisotropic Segmental Motion to Chain Dynamics in *cis*-1,4-Polybutadiene†

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ABSTRACT: Solid-state NMR coherent averaging methods and variable-field experiments are combined to illustrate the contribution of anisotropic segmental motion to the chain dynamics of *cis*-1,4-polybutadiene at 25 °C. The macromolecular motion as observed by NMR is shown to be best modeled as rapid anisotropic segmental motion that is spatially inhibited by chain constraints. The lifetime and spatial distributions of these constraints are not reflected in either conventional or coherent averaging NMR experiments for high molecular weight ($\bar{M}_w \sim 3.5 \times 10^5$) *cis*-1,4-polybutadiene.

Introduction

Solid-state NMR spectroscopy has been a valuable method for the characterization of macromolecular dynamics for many years.[1] The application of NMR coherent averaging methods[2] to probe chain dynamics has led to a renewed emphasis on describing the dynamic processes in terms of *both* the rate and angular amplitude of motion.[3–6]

cis-1,4-Polybutadiene has been the subject of many previous investigations. In our initial contribution in this area,[7] we briefly reviewed the previous ^{1}H[4,8–15] and ^{13}C[16,17] NMR results. These investigations have not produced a self-consistent model of the motion, and there is some controversy as to the relative importance of entanglements in interpreting the NMR results. Models have been proposed that attribute the residual line broadening apparent in both the ^{13}C and ^{1}H conventional NMR spectra and/or the spin–lattice relaxation behavior to (1) incomplete motional narrowing arising from insufficiently fast, spatially isotropic motion, (2) spin diffusion between rapidly isotropically reorienting chain segments between entanglements and the entanglements which are temporally and spatially hindered,[14] and (3) anisotropic segmental motion arising from spatial restrictions imposed by entangle-

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