

Evaluation of End Groups in Poly(Methyl Methacrylate-co-Styrene) by ^{13}C NMR

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Summary

The carbonyls of the various benzoate end groups in poly(methyl methacrylate-co-styrene) prepared with benzoyl-carbonyl- ^{13}C peroxide give rise to discrete and characteristic signals in the 62.9 MHz ^{13}C NMR spectra of the copolymers. Thus, by integration of the spectra, it is possible to estimate the relative reactivity of benzoyloxy radicals towards styrene and methyl methacrylate. In addition, information on the amount of initiator consumed in other processes such as transfer to initiator and primary radical termination can be obtained.

Introduction

The analysis of ^{13}C NMR spectra of polystyrene (PS) prepared with benzoyl-carbonyl- ^{13}C peroxide has been reported previously (1). In the course of that study, the ^{13}C NMR spectra of a variety of model compounds were also examined and it was established that the carbonyl carbons of primary, secondary, tertiary, and aromatic benzoates have characteristic chemical shifts. Moreover, it was found that the chemical shifts of the benzoate carbonyls of PS end groups are sensitive to the nature and stereochemistry of the penultimate and penpenultimate monomer units. Thus, it was possible to distinguish the benzoate groups incorporated by (a) tail addition to styrene, (b) head addition to styrene, (c) transfer to initiator or primary radical termination, and (d) aromatic substitution (1).

More recently, Bevington et al. (2,3) have determined that the relative reactivity of cyanoisopropyl radical towards various monomers can be determined by examining the ^{13}C NMR spectra of copolymers prepared with azobis(isobutyronitrile- $\beta\beta$ - $^{13}\text{C}_2$). They also reported (2,3) that an attempt to use a similar procedure to evaluate the relative reactivity of benzoyloxy radicals (from benzoyl-carbonyl- ^{13}C peroxide) towards methyl methacrylate (MMA) and styrene (S) was unsuccessful because the signals due to the carbonyls of the various benzoate end groups were not resolved under the conditions of their experiment. They considered this surprising (3) in the light of our earlier findings (see above).

In the course of work aimed at evaluating the kinetics and mechanism of copolymerization of S and MMA by ^{13}C NMR, we have prepared a number of copolymers using various carbon-13 labelled initiators. Examination of the 62.9 MHz ^{13}C NMR spectra of poly(methyl methacrylate-co-styrene) (PMMA) prepared with 90% enriched benzoyl-carbonyl- ^{13}C peroxide showed that the signals due to the labelled carbons of the various types of end groups are resolved and are readily distinguished. In this paper we give a preliminary report on this aspect of our work.

Results and Discussion

The region 164.5-166.5 ppm of the ^{13}C NMR spectra of PS, two samples of PMMAS, and poly(methyl methacrylate) (PMMA), all prepared with benzoyl-carbonyl- ^{13}C -peroxide as the initiator, are shown in Figs. 1a-d respectively.

The spectrum of PMMA, like that of PS (1), displays two signals attributable to the carbonyls of primary benzoates (formed by tail addition of $\text{PhCO}_2\cdot$ to monomer). However, in the PMMA spectrum, these signals appear at slightly higher field and show less fine structure than the corresponding signals in the PS spectrum (signals at 165.80 and 166.00 ppm in PMMA vs. 166.25 and 166.35 ppm in PS - compare Figs. 1a and d). In addition, there are signals centred at 165.05 ppm, in the region characteristic of the carbonyls of tertiary benzoates (1) (the benzoate carbonyl of the model compound $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)\text{O}_2\text{CPh}$ gives a signal at 165.2 ppm). Tertiary benzoates can arise by head addition to MMA, by transfer to initiator, or by primary radical termination. The intensity

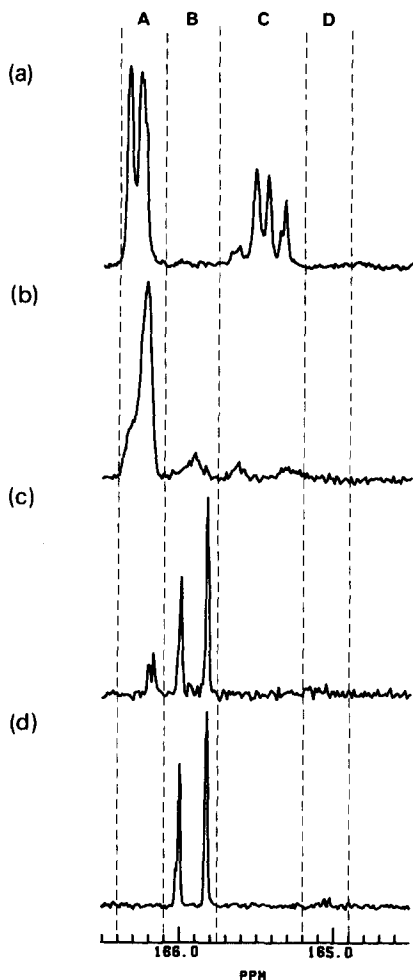


Fig. 1. Region 164.5-166.5 ppm of 62.9 MHz ^{13}C NMR (CDCl_3) spectra of (a) PS (1), PMMAS prepared with a monomer feed ratio (MMA:S) of (b) ca. 1:1 or (c) 20:1 (refer table 1), and (d) PMMA. Conditions for running the spectra have been described previously (1). Chemical shifts in the text are given to the nearest 0.05 ppm.

Peak assignments are as follows:

- A. $\text{Ph}\overline{\text{C}}\text{O}_2\text{CH}_2\text{CH}(\text{Ph})-$
- B. $\text{Ph}\overline{\text{C}}\text{O}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)-$
- C. $\text{Ph}\overline{\text{C}}\text{O}_2\text{CH}(\text{Ph})\text{CH}_2-$
- D. $\text{Ph}\overline{\text{C}}\text{O}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)\text{CH}_2-$

A and B are abbreviated as $\text{PhCO}_2\text{-S-}$ and $\text{PhCO}_2\text{-MMA-}$ respectively in the text.

of the signals in this region corresponds to ca. 5% of total end groups which is in accordance with our earlier finding, that benzoyloxy radical adds to MMA to give tail and head addition products in the ratio 1:0.07 (4) and indicates that the extent of transfer to initiator is minimal under the polymerization conditions (60°C, 50% (v/v) benzene, 0.2M initiator).

On the basis of the homopolymer spectra we can assign the signals due to the carbonyls of $\text{PhCO}_2\text{-S-}$ and $\text{PhCO}_2\text{-MMA-}$ end groups in the spectra of PMMAS. In the spectrum of the 1:1 copolymer (Fig. 1b), signals due to the $\text{PhCO}_2\text{-S-}$ ends appear as a peak with a maximum at 166.20 ppm and a shoulder at 166.35 ppm. In the case of the 20:1 copolymer (Fig. 1c), the $\text{PhCO}_2\text{-S-}$ ends give rise to a group of peaks centred at 166.15 ppm. For the latter copolymer, the majority of benzoates at styryl ends will be of the form $\text{PhCO}_2\text{-S-MMA-}$ (as a consequence of the large excess of MMA over S in the feed, most $\text{PhCO}_2\text{-S}^{\bullet}$ radicals should add to MMA rather than S).

It would seem reasonable, given the spectrum of benzoate end groups in PS (Fig. 1a) and in the 20:1 copolymer (Fig. 1c), to attribute the shoulder at 166.35 ppm in the spectrum of the 1:1 copolymer (Fig. 1b) to one half of the end groups of the form $\text{PhCO}_2\text{-S-S-}$. The other half of these end groups and the $\text{PhCO}_2\text{-S-MMA-}$ ends appear as the main peak at 166.20 ppm. On this basis we estimate the ratio of $\text{PhCO}_2\text{-S-MMA-}$ to $\text{PhCO}_2\text{-S-S-}$ ends in the 1:1 copolymer to be $1.7 \pm 0.5:1$. Confirmation of our assignments awaits the preparation of appropriate model compounds. It can be calculated (table 1) that if the relative reactivity of $\text{PhCO}_2\text{-S}^{\bullet}$ is the same as that of polystyryl radical towards MMA and S, then the ratio of $\text{PhCO}_2\text{-S-MMA-}$ to $\text{PhCO}_2\text{-S-S-}$ ends in the 1:1 copolymer will be approximately 2:1 (refer table 1).

In the case of the 1:1 copolymer, the carbonyls of the $\text{PhCO}_2\text{-MMA-}$ ends give rise to a small broad peak centred at 165.90 ppm. On the other hand, in the 20:1 copolymer, the pattern of signals due to these end groups is identical to that seen in the spectrum of PMMA (compare Figs. 1c and 1d). This is as expected since most benzoates at methacrylyl ends in the 20:1 copolymer should be of the form $\text{PhCO}_2\text{-MMA-MMA-}$, just as in PMMA.

Table 1. Distribution of Primary Benzoate End Groups in Poly(methyl methacrylate-co-styrene)^a

polymer MMA:S	$[\text{MMA}]_0$ M	$[\text{S}]_0$ M	$\text{PhCO}_2\text{-S-S-}$ %	$\text{PhCO}_2\text{-S-MMA-}$ %	$\text{PhCO}_2\text{-MMA-S-}$ %	$\text{PhCO}_2\text{-MMA-MMA-}$ %
(A) calculated ^b						
1:1	2.36	2.18	29	61	7	4
20:1	4.48	0.22	(0.2)	16	4	80
(B) found						
1:1 ^c	2.36	2.18	86		14	
20:1 ^d	4.48	0.22	19		81	

(a) Prepared in benzene- d_6 with an initiator concentration of 0.05 M.

(b) Calculated using the SOCK program (5) and on the basis of benzoyloxy radical adding to S 9 times faster than it adds to MMA (4), copolymerization reactivity ratios for S and MMA of 0.52 and 0.46 (6), and the following conversions.

(c) At 40% conversion and a reaction time of 720 min.

(d) At 85% conversion and a reaction time of 960 min.

The spectrum of the 1:1 copolymer also shows signals in the regions appropriate for secondary and, perhaps, tertiary benzoate carbonyls. These may be attributed to those end groups which arise by head addition plus those from transfer to initiator or primary radical termination. However, additional model compounds and spectra with better signal to noise are required to complete the assignment of peaks in these regions.

The relative intensities of the signals due to the carbonyls of PhCO₂-S- as opposed to PhCO₂-MMA- ends shows that S is substantially more reactive than MMA towards benzoyloxy radical (4,7). Integration of the NMR spectra indicates a relative reactivity (S:MMA) of ca. 9:1 which is in agreement with our previous finding of 9.1:1 (4) using the radical trapping technique.

A more precise estimate of the relative reactivity might be obtained by examining the ¹³C NMR of low conversion copolymers prepared using a wider range of initial monomer concentrations. However, it should be pointed out that the radical trapping technique (4,8) is a superior method for evaluating relative reactivities in that, with current instrumentation, the errors inherent in integrating a hplc trace are substantially less than those involved in integrating an NMR spectrum. Moreover, in the case of the trapping technique, the reaction products, being of low molecular weight, can be separated and fully characterized using conventional techniques.

Nevertheless, the NMR method remains extremely valuable in that it gives information on the other processes in which the initiator may become involved (eg. transfer to initiator and primary radical termination) (1,9). As a consequence, the use of a labelled initiator also offers many advantages in the study of polymerization kinetics by NMR since it permits such factors as the initiator efficiency and the rate of initiation to be evaluated concurrently with the rates of monomer disappearance and polymer formation. Full details of our studies on the kinetics of initiator incorporation during polymerizations carried out with benzoyl peroxide and other initiators will be published in the near future.

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