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Fate of the Initiator in the Azobis(isobutyronitrile)-Initiated Polymerization of Styrene

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ABSTRACT: The initiator-derived residues in polystyrene prepared by using azobis(isobutyronitrile-α-^{13}C) as the initiator have been identified and quantified by ^{13}C NMR. For low-conversion polymers the only initiator fragments present are those incorporated during the initiation step (i.e., by tail addition to monomer). Contrary to some recent reports, primary radical termination and transfer to initiator were found to be of little importance in AIBN-initiated styrene polymerization. These processes account for less than 2% of end groups in low-conversion (8%) polymers prepared in bulk with initiator concentrations in the range 0.01–0.2 M. In high-conversion (85%) polymers prepared with a high (0.2 M) initiator concentration the copolymerization of methacrylonitrile formed from the initiator can be detected.

Introduction

There is evidence to show that the stabilities of polystyrenes prepared by free radical processes are dependent on the methods used in their preparation and, in particular, the types of initiator used.[1] However, the differences in the polymer structure which might account for the observed variation in properties are unclear.

As a first step toward solving this problem we have investigated the selectivity of the initiation process by examining the interaction of alkoxy, benzoyloxy, and phenyl radicals with styrene by using a radical scavenging technique.[2] The method is, however, not as suitable for looking at the reactions of alkyl radicals (e.g., cyanoisopropyl) and does not give information on the other ways by which initiator fragments can be incorporated into the polymer structure (i.e., primary radical termination and transfer to initiator). To obtain this information we required a method which enables the initiator-derived functionality in the polymer to be determined directly.

A variety of methods (e.g., radiochemical labeling[3-6] and ^1H NMR[7]) have been used for determining the initiator residues incorporated into vinyl polymers during their preparation. These methods, however, only give information as regards the number of such groups. They are, in general, not sufficiently sensitive to the environment of the initiator-derived functionality for one to be able to say, with any degree of certainty, how it was incorporated into the polymer.

Recently, we demonstrated a ^{13}C NMR technique by which the nature of the benzoyloxy groups in polystyrene prepared with benzoyl-*carbonyl*-^{13}C peroxide as the initiator could be evaluated.[8] Thus, the benzoate end groups

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incorporated by initiation and by transfer to initiator plus primary radical termination were identified and quantified. At about the same time, Bevington et al.[9] showed that the end groups of polymers prepared with azobis(isobutyronitrile-β,β-$^{13}C_2$) could be examined by ^{13}C NMR. A similar approach has also been applied in the investigation of the mechanism of the polymerization of olefins by ^{13}C-labeled organometallic reagents.[10] In this paper we wish to report our findings regarding the nature of the initiator-derived residues in polystyrene prepared with azobis(isobutyronitrile-α-^{13}C) (AIBN-α-^{13}C).

Experimental Section

General Data. General experimental details including the method used for polymer preparation and characterization are given elsewhere.[8]

AIBN-α-^{13}C. ^{13}C-labeled AIBN was prepared from 90% enriched acetone-2-^{13}C (Merck, Sharpe, and Dohme) by using the standard procedure.[11] ^{13}C NMR (62.9 MHz) δ 68.1 (CCN).

Oligomerization Experiments. (a) The procedure developed by Rizzardo and Solomon was employed.[12,13] A solution of ferric chloride hexahydrate (110 mg) and AIBN-α-^{13}C (32 mg) in styrene (50 mL) and *N,N*-dimethylformamide (50 mL) was heated in vacuo at 100 °C for 4 h then cooled and the solvent evaporated under reduced pressure. The residue was taken up in ethyl acetate, washed with water, dried ($MgSO_4$), and evaporated to leave a colorless oil (200 mg). The oligomers (**1**, n = 2–10) were isolated by high-performance liquid chromatography (HPLC) using an Altex Ultrasphere 10 mm × 25 cm ODS column and acetonitrile/water as the eluant (70% for 5 min, gradient to 100% over 10 min). The relative yield of the oligomers (**1**) was as follows (data are in the order: n, normalized yield (%) determined by HPLC assuming $\epsilon_{254} \propto n$): 2, 34; 3, 21; 4, 18; 5, 9; 6, 6; 7, 4; 8, 3; 9, 2; 10, 2. A portion of the ^{13}C NMR spectra of **1**, n = 5–8, is shown in Figure 1a.

(b) A solution of AIBN (165 mg) in styrene (1 mL) and toluene (5 mL) was heated at 98 °C for 3 h. The solvent was then removed under reduced pressure. The low molecular weight fraction (n < 4) was analyzed by GCMS (chemical ionization using methane) using a 10% Silar 10C (2 m × 2 mm) column and helium (25 mL min^{-1}) as carrier gas and a temperature program 50–250 °C at 10 °C min^{-1} (a similar experiment was conducted with AIBN-d_{12}—the product distribution was unchanged). The following compounds were observed (relative peak area given in parentheses, peaks listed in order of elution): **2**, n = 0 (34.6); **4**, n = 1 (5.6); **5**, n = 1 (2.8); **2**, n = 1 (9.1); **4**, n = 2 (4.5); **5**, n = 2 (1.2); **3**, n = 1, m = 1 (17.5); **2**, n = 2 (3.0), **3**; n = 1, m = 1 (14.9); **4**, n = 3 and **2**, n = 2 (4.8); **4**, n = 3 (2.0). Note that two diastereomers of each **3**, n = 1, m = 1, **2**, n = 2, and **4**, n = 3 were observed. The oligomers (**2**, n = 1), (**3**, n = 1, m = 1), (**3**, n = 1, m = 2), and a mixture of **2**–**5**, **n** = 4–10 were isolated by HPLC (conditions as above).

2,2,5,5-Tetramethyl-3-phenylhexanedinitrile (2, n = 1): mp 118–120 °C [lit.[14] mp 121–122 °C]; ^1H NMR (90 MHz) δ 0.97, 1.08, 1.35, 1.45 (4 × s, 12 H, CH_3), 2.20 (br d, 2 H, J = 7 Hz, CH_2), 2.75 (br t, 1 H, J = 7 Hz, CH), 6.9–7.4 (m, 5 H, ArH); ^{13}C NMR δ 25.2, 26.9 (2 C) and 28.3 (CH_3), 32.7 (C5), 37.1 (C2), 42.4 (C4), 51.5 (C3), 124.1 (CN), 128.1, 128.8, 129.0, and 139.3 (ArC).

2,2,7,7-Tetramethyl-4,5-diphenyloctanedinitrile (3, n = 1, m = 1). An equimolar mixture of the two diastereomers: ^1H NMR (250 MHz) δ 0.84, 0.99, 1.07, 1.12 (4 × s, 24 H, CH_3), 1.58 (dd, J = 3, 14 Hz, 1 H, CH_2), 1.75 (dd, J = 7, 14 Hz, 1 H, CH_2), 1.95 (dd, J = 7, 14 Hz, 1 H, CH_2), 2.18 (dd, J = 2, 14 Hz, 1 H, CH_2), 2.97 (m, 1 H, CH), 3.10 (m, 1 H, CH), 6.9–7.4 (m, 20 H, ArH). Decoupling experiments showed the multiplets at δ 1.58 and 1.75 to be coupled to that at δ 3.10 and the multiplets at δ 1.95 and 2.18 to be coupled to that at δ 2.97.

2,2,9,9-Tetramethyl-4,5,7-triphenyldecanedinitrile (3, n = 1, m = 2). The compound was isolated as two fractions in the ratio 1:3. Fraction 1 was a single diastereomer: ^1H NMR (250 MHz) δ 0.78, 0.88, 0.99, 1.09 (4 × s, 12 H, CH_3), 1.6–3.0 (m, 9 H, CH and CH_2), 6.7–7.4 (m, 15 H, ArH); ^{13}C NMR δ 26.5, 27.4, 27.5, and 27.9 (CH_3), 31.4 and 31.7 (CCN), 40.1, 41.1, 44.5, 48.5, 49.2, and 49.7 (CH and CH_2), 124–130 and 143–144 (CN and ArC). Fraction 2 was an equimolar mixture of the other three diastereomers: ^1H NMR (250 MHz) δ 0.85, 0.90, 0.91, 0.93, 0.95, 1.00, 1.03, 1.07, 1.12, 1.15, 1.20, 1.24 (12 × s, 12 H, CH_3), 1.5–2.2 (m, 6 H, CH_2), 2.2–3.2 (m, 3 H, CH), 6.7–7.4 (m, 15 H, ArH); ^{13}C NMR δ 26.7, 26.9 (3 C), 27.1, 27.4, 27.5 (2 C), 27.7, 27.9, 28.1, and 28.3 (CH_3), 31.6, 31.7, 32.0, 32.1, and 32.5 (2 C) (CCN), 40.4 (2 C), 40.5, 41.2, 41.7, 43.2, 43.7, 43.9, 44.2, 45.3, 45.9, 47.7, 48.3, 49.1, 49.2, 49.6, 49.7, and 50.7 (CH and CH_2), 124–130 and 140–146 (CN and ArC).

Other Model Compounds. 2,2-Dimethyl-3-phenylpropanenitrile (6). Isobutyronitrile was added to a stirred solution of lithium diisopropylamide (prepared by addition 0.85 M *n*-butyl lithium in hexane (19 mL) to diisopropylamine (1.6 g) in ether (10 mL) and tetrahydrofuran (10 mL)) at −78 °C. After 20 min at −78 °C 1-chloro-1-phenylethane (2.0 g) was added. The mixture was maintained at −78 °C for a further 20 min and then allowed to warm to room temperature during 2 h whereupon it was poured into ice–water and extracted with dichloromethane. The combined extracts were washed with water and brine, dried ($MgSO_4$), and evaporated to leave 2.0 g (90%) of an oil which was fractionated under vacuum: bp 80 °C (0.3 mmHg) [lit.[15] bp 262 °C (760 mmHg)]; ^{13}C NMR δ 17.1 (CH_3), 25.1 and 26.3 (CH_3), 37.1 (C2), 47.9 (C3), 124.4 (CN), 127.2, 128.3, 128.4, and 141.4 (ArC).

2,2-Dimethyl-3,5,7-triphenylheptanenitrile (7, n = 2). A solution of chalcone (35 g) in ether (350 mL) was added to a stirred solution of 0.25 M 2-phenylethylmagnesium bromide in ether (100 mL) at 0 °C. After 2 h at 0 °C the mixture was poured onto ice, acidified by the addition of ammonium chloride, and extracted with ether. The combined ether extracts (ca. 500 mL) were washed with 10% sodium carbonate and brine, dried ($MgSO_4$), and concentrated to ca. 50 mL. This solution was then cooled to −4 °C to afford a precipitate of 1,3,5-triphenylpentan-1-one (26 g, 49%): mp 80–81 °C (EtOH); ^1H NMR (90 MHz) δ 1.9–2.2 (m, 2 H, CH_2), 2.3–2.6 (m, 2 H, CH_2), 3.2–3.5 (m, 3 H, $CHCH_2$), 7.0–7.5 and 7.8–8.0 (m, 15 H, ArH); IR ($CHCl_3$) 1680 cm^{-1}; Anal. ($C_{23}H_{22}O$): C, H.

Sodium borohydride (2 g) was added to a solution of 1,3,5-triphenylpentanone (5.2 g) in absolute ethanol (500 mL) and the mixture was stirred at room temperature for 3 days. Workup in the usual manner afforded 1,3,5-triphenylpentan-1-ol (5.0 g, 96%) as a mixture of two diastereomers in the ratio ca. 3:2. This alcohol (5.0 g) in chloroform (10 mL) was treated with thionyl chloride (2.1 g, 1.3 mL) and the resulting solution was allowed to stir for 2 h at room temperature. The chloroform and excess thionyl chloride were then evaporated and the residue was taken up in dichloromethane, washed with saturated sodium bicarbonate solution and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure to leave 1-chloro-1,3,5-triphenylpentane (5.0, 94%) as a pale yellow oil. HPLC and ^1H NMR showed this material to be contaminated with ca. 5% of 1,3,5-triphenylpent-1-ene. Pure samples of the two diastereomers of the chloro compound were isolated by preparative HPLC: ^1H NMR (250 MHz) δ 1.7–2.1 (m, 2 H), 2.3–2.6 (m, 5 H), 4.60 (dd, J = 1, 7 Hz, 1 H, CHCl), 7.0–7.4 (m, 15 H, ArH). The second eluted diastereomer had ^1H NMR (250 MHz) 1.9–2.1 (m, 2 H), 2.14 (ddd, J = 3, 11, 13 Hz, 1 H), 2.4–2.6 (m, 3 H), 2.0–2.2 (m, 1 H), 2.46 (dd, J = 3, 11 Hz, CHCl), 7.0–7.4 (m, 15 H, ArH).

The crude 1-chloro-1,3,5-triphenylpentane (4.6 g) was subjected to the conditions described above for the preparation of **6** to afford a mixture (5.2 g) comprising unchanged chloro compound (65%), the required compound (**7**, n = 2) (30%), and a number of unidentified byproducts (5%). **7**, n = 2 was a mixture of the two diastereomers in the ratio 2:1 which were separated by HPLC using 90% acetonitrile as eluant. The first eluted diastereomer was a white crystaline solid: mp 109–110 °C; ^1H NMR (90 MHz) δ 1.10 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.7–2.8 (m, 8 H), 6.9–7.4 (m, 15 H, ArH); ^{13}C NMR δ 25.0 and 26.8 (CH_3), 33.4 and 35.8 (CH_2), 36.8 (C2), 38.8 (CH_2), 42.6 (C5), 51.9 (C3), 124.7 (CN), 126–129, 138.9, 142.3, and 145.3 (ArC); IR ($CHCl_3$) 2235 cm^{-1}; CIMS (CH_4) m/z 368 (M + 1); Anal. ($C_{27}H_{29}N$) C, H. The second eluted diastereomer was a colorless oil: ^1H NMR (90 MHz) δ 1.00 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.7–2.8 (m, 8 H), 6.9–7.4 (m, 15 H, ArH); ^{13}C NMR δ 25.2 and 26.6 (CH_3), 33.7 (CH_2), 36.5 (C2), 37.6 and 39.7 (CH_2), 43.1 (C5), 51.3 (C3), 124.7 (CN), 126–129, 139.1, 142.3, and 144.0 (ArC); IR ($CHCl_3$) 2235 cm^{-1}; CIMS (CH_4) m/z 368 (M + 1).

Table I
Initiator-Derived Functionality in Polystyrene Samples A–D

polymer	[I][a]	molecular weight	conversion[b]	"normal" end groups/ molecule[c]	copolymerized MAN/molecule[c]
A[d]	0.2	22 000[f]	8%	1.7	*h*
B[d]	0.01	112 000[f]	8%	1.8	*h*
C[d]	0.2	48 000[g]	85%	2.1	0.2
D[e]	0.01	23 000[f]	60%	2.1	trace

[a] Initial concentration of AIBN. [b] On the basis of yield of isolated polymer. Polymers A, B, C, and D were prepared by using reaction times of 50, 200, 960, and 1200 min, respectively. [c] Error in the relative number of end groups per molecule is ±10%. [d] Prepared in bulk. [e] Prepared in solution (20% styrene in benzene (v/v)). [f] GPC number average molecular weight; $\bar{M}_w/\bar{M}_n \simeq 1.7$. [g] $\bar{M}_w/\bar{M}_n \simeq 5.7$. [h] Not detectable.

Table II
^{13}C Chemical Shifts of Model Compounds

compd	carbon	shift,[a] δ
1, $n > 4$	$(CH_3)_2C(CN)CH_2$-	31.5-32.1[b]
2, $n = 1$	$(CH_3)_2C(CN)CH_2$-	32.7
2, $n = 1$	$(CH_3)_2C(CN)CHPh$-	37.1
tetramethyl-succinonitrile	$(CH_3)_2C(CN)$-	39.6
AIBN	$(CH_3)_2C(CN)$-	68.1
styrene/MAN (4:1) copolymer	$-CH_2C(CH_3)(CN)CH_2$-	33.7-36.3
6	$(CH_3)_2C(CN)CHPh$-	37.1
7, $n = 1$[c]	$(CH_3)_2C(CN)CHPh$-	36.6
7, $n = 2$[d]	$(CH_3)_2C(CN)CHPh$-	36.5, 36.8
8	$(CH_3)_2C(O)NH$-	35.6
9	$(CH_3)_2C(O)NH$-	35.6

[a] Chemical shift relative to internal $(CH_3)_4Si$. [b] See Figure 1a. [c] ^{13}C NMR data for this compound were provided by Dr. A. K. Serelis. [d] Compound is diastereomeric.

Styrene/MAN Copolymer. A solution of AIBN (160 mg) in freshly distilled styrene (8.0 mL) and MAN (2.0 mL) was degassed by using three freeze–thaw cycles at 10^{-6} mmHg and then heated in vacuo at 60 °C for 2 h. The polymer was precipitated in methanol then twice redisolved in benzene and precipitated in methanol to afford, after drying, 0.72 g of Styrene/MAN copolymer, M_n (GPC) ca. 30 000 (relative to polystyrene).

Polystyrene NMR. The 62.9-MHz ^{13}C NMR spectra of polystyrene samples A, B, C, and D 25% (w/v) in $CDCl_3$ were accumulated into 32K of memory using a spectral width of 12 195.122 Hz. A relaxation delay of 17.7 s, a pulse width of 10 μs, and an acquisition time of 1.34 s were used. For the suppression of nuclear Overhauser enhancement the ^{1}H broad-band decoupler was off during the relaxation delay and on during acquisition. In processing, the FID was zero filled out to 64K data points and an exponential line broadening of 2.0 (Figure 2) or 0.5 Hz (Figure 1) was applied. For good signal to noise, spectra typically required the accumulation of 3000–10 000 transients.

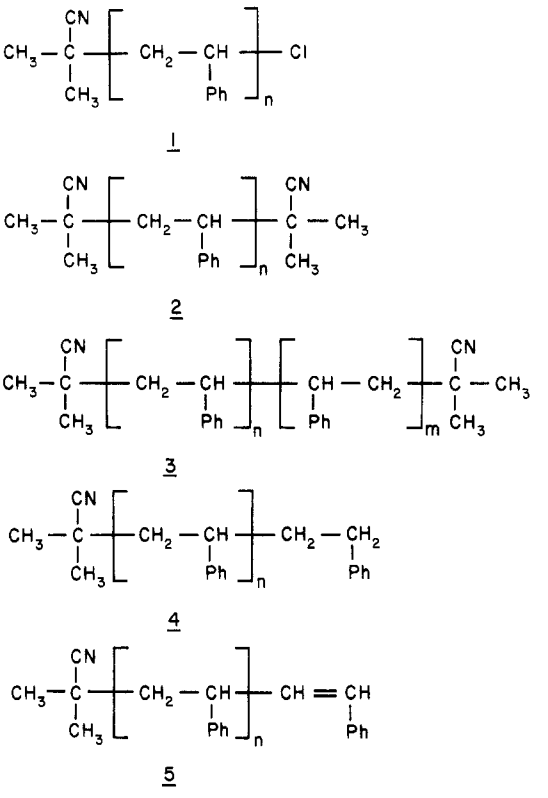
T_1s were calculated using a nonlinear, three-parameter, curve-fitting program and data acquired using a standard inversion–recovery sequence.

Results

Polystyrene samples were prepared by using AIBN-α-^{13}C at 60 °C in bulk (A–C) or in benzene solution (D) (refer Table I) and were purified by precipitation with methanol. Three precipitations were sufficient to remove tetramethylsuccinonitrile and residual AIBN. Molecular weights were determined by GPC.

To assist in assigning the resonances to the various types of groups described above, a number of model compounds have been synthesized (Table II, Chart I). A series of oligomers (1) was prepared by decomposing AIBN-α-^{13}C at 100 °C in styrene/dimethylformamide solution containing ferric chloride as a free radical trapping agent[12] and isolated by reverse-phase HPLC. The reaction affords almost exclusively the oligomers (1), however, small amounts (<2%) of the terminally unsaturated oligomers

Chart I



(5) were detectable by HPLC.

Another oligomerization experiment was investigated as a means of obtaining low molecular weight compounds with end groups from primary radical termination. This involved decomposing AIBN in styrene in toluene at 98 °C to give a mixture of 2–5. However, analysis of the low molecular weight fraction (n = 0–2) showed that the reaction gave less than 15% of products from primary radical termination (value based on the yields of **2**, n = 1, **3**, n = 1, m = 1, and **3**, n = 1, m = 2). The NMR analysis of higher molecular weight products separated by preparative HPLC was also consistent with there being little primary radical termination (on the basis of the intensity of resonances in the region 36–37 ppm). The reaction also proved to be less selective than previously suggested,[16] in that a significant fraction (10–20%) of the products, i.e., **4** and **5**, were formed by disproportionation. It was established that these compounds (**4** and **5**) were largely derived from disproportionation between oligostyryl radicals, rather than from the reaction of oligostyryl radicals with cyanoisopropyl radicals or with AIBN, by conducting the oligomerization with AIBN-d_{12} (99% enriched) as the initiator. In that experiment the product distribution was unchanged and the deuterium enrichment of the products **4**, n = 0–2, was <5%.

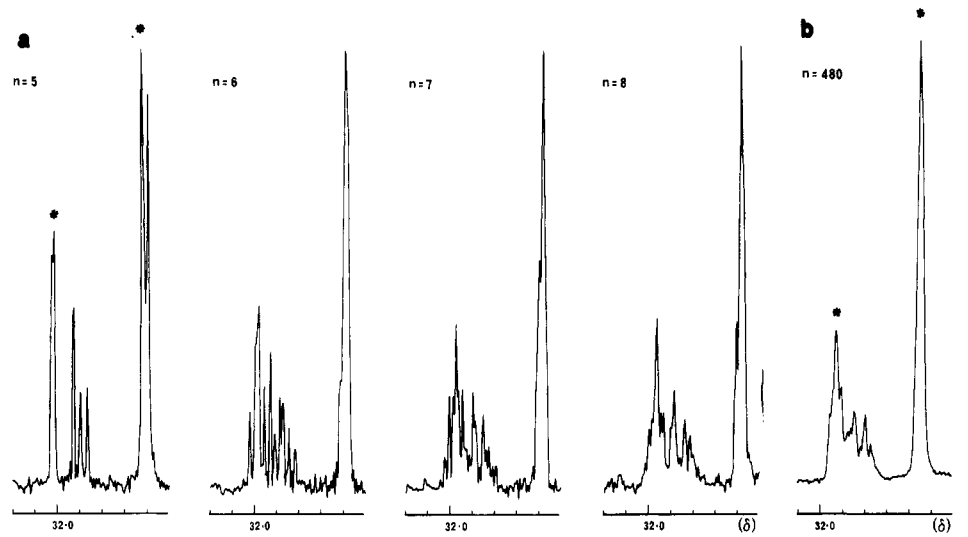
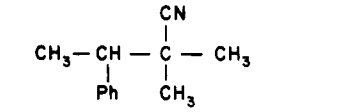
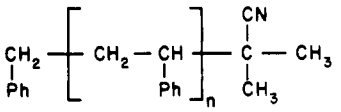


Figure 1. Region δ 31.5–32.2 of the ^{13}C NMR spectra of (a) the oligomers 1 (n = 5–8) and (b) polymer C (refer Table I). T_1 measurements (see text) were carried out on the resonances marked with an asterisk.

The model compounds, **6** and **7**, n = 2, which have end groups of the type that would be formed by primary radical termination, were available from the reaction of cyanoisopropyl anion with the corresponding chloro compounds (see Experimental Section).



6



7

For quantitative work the NMR spectra of the polystyrene samples were obtained using a long pulse delay (17 s with 40° pulse angle) such that the observed peak intensities were not influenced by relaxation phenomena. In order to obtain an estimate of the absolute number of end groups per molecule the signals due to the enriched end groups were integrated relative to the polystyrene backbone carbons. The NMR spectra were also recorded with inverse-gated decoupling so as to eliminate nuclear Overhauser enhancement.

The T_1s of the quaternary carbons in the cyanoisopropyl end groups of polystyrene (refer Figure 1b) have been determined as ca. 4 s (low-field resonance) and 5 s (high-field resonance, refer Figure 1). This compares with T_1s of ca. 8.7 and 9.1 s, respectively, in the pentamer (**1**, n = 5). Due to the possibility that errors may be introduced into the measurements by determining the T_1 of an envelope rather than a single peak we attach no significance to the apparent variation in T_1 with end group stereochemistry at this stage. By way of contrast, we have found that the T_1s of the quaternary carbons in a 4:1 styrene/MAN copolymer are ca. 1.5 s. This result, that terminal groups have longer T_1s than similar groups within polymer chains, is in line with previous findings.[17]

Spectra (see Figure 2) have also been obtained by using the pulse sequence described by Bendall et al.[18] which results in the effective cancellation of all signals due to carbons bearing hydrogen atoms. These experiments demonstrate that the signals attributed to the enriched initiator residues are indeed due to quaternary carbon atoms and confirm that no resonances are hidden underneath the envelope due to the methylene and methine carbons of the polystyrene backbone. Other spectra (see Figure 2) were obtained by employing the backbone suppression technique, recently demonstrated by Johns et al.,[13] which makes use of the fact that end group carbons have long relaxation times (T_2s) relative to the backbone carbons. It is notable that the signals appearing at 34–36 ppm in the spectrum of polymer C (Figure 2, rightmost spectrum) are also reduced in intensity with respect to those due to the "normal" end group carbons.

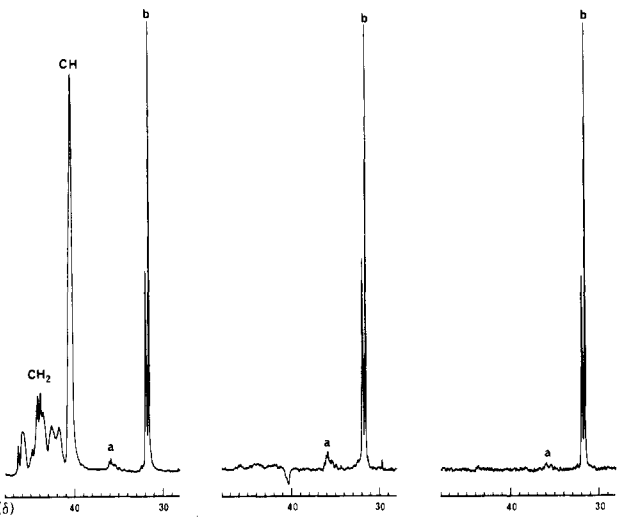


Figure 2. Region δ 28.0–45.0 of the ^{13}C NMR spectra of polymer C. From left to right the spectra are as follows: the normal spectrum obtained using 17-s pulse delay and 40° pulse angle; the spectrum obtained by using "quaternary carbon only" pulse sequence of Bendall et al.;[18] and the spectrum obtained using the sequence[13] $\pi/2$–τ–π–τ–acquire, with τ = 0.7 s. The signals at a and b are assigned to the "normal end groups" and to copolymerized MAN, respectively.

The same signals are enhanced in spectra recorded with a short (1 s) pulse delay (see, for example, center spectrum of Figure 2). This indicates that the carbons have a relatively short relaxation time which is consistent with their being backbone carbons (signals are attributed to copolymerized methacrylonitrile (MAN)) rather than end group carbons (see above).

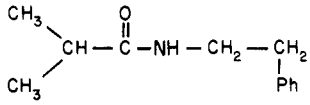
Discussion

The literature[3-6,19-26] suggests a number of ways by which

the cyanoisopropyl groups from AIBN might become incorporated into a vinyl polymer. These include the following processes: (a) initiation (addition to monomer); (b) primary radical termination (coupling with the growing polymer radical); (c) transfer to initiator (by cyanoisopropyl group transfer); (d) formation of methacrylonitrile which can then undergo copolymerization. In addition, there is some evidence that these radicals, which can be considered as a hybrid of two resonance forms [$(CH_3)_2C(\cdot)C{\equiv}N \leftrightarrow (CH_3)_2C{=}C{=}N\cdot$], may react to give either a cyanoisopropyl or an unstable keteniminyl group.[4] The ^{13}C NMR spectra of model compounds (see Table II) show that the quaternary carbons in the functionality introduced by the processes (a–d) all have distinctive chemical shifts.

The ^{13}C NMR spectra show that the only cyanoisopropyl groups incorporated into "low-conversion" polystyrene (samples A and B) in significant amounts are those which arise during the initiation reaction (by tail addition to styrene). The quaternary carbon of this end group gives rise to a complex pattern comprising a relatively sharp peak centered at 31.6 ppm and a broader envelope covering the region 31.8–32.1 ppm (see Figure 1b). Integration shows that there are approximately equal proportions of meso and *dl* chain ends. However, a comparison of the ^{13}C NMR of the oligomers and the polymers shows that the resonances contain stereochemical information regarding groups eight or more monomer residues removed (Figure 1).

In accord with the recent work of Bevington et al.[9] we can find no evidence of keteniminyl end groups in the isolated polymer. In addition, we have considered the possibility that the polymers might contain isobutyramide end groups which could arise from the hydrolysis of keteniminyl groups during work up. The model compounds (8 and 9) were prepared from the corresponding amines and isobutyroyl chloride. However, no isobutyramide end



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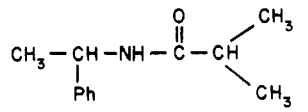

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groups, as indicated by an absence of signals in the region 35–36 ppm, could be detected in the polystyrene samples A, B, and D.[27] We conclude, therefore, that if a significant fraction of initiation or termination occurs so as to form a keteniminyl residue, the groups do not survive the polymerization conditions.

Resonances attributable to copolymerized methacrylonitrile (MAN) occurring at 34–36 ppm (identified by comparison with the spectrum of a styrene/MAN copolymer) are only observed in the "high-conversion" polymer C (see Figure 2). MAN may come from several sources. One is the cage reaction of cyanoisopropyl radicals. The initiator efficiency for AIBN[28] is such that ca. 40% of cyanoisopropyl radicals are lost through self-reaction in the cage, of these ca. 10% can be expected to undergo disproportionation to give a molecule each of MAN and isobutyronitrile.[29] If we assume that all of the cyanoisopropyl radicals that escape the cage will initiate polystyrene chains, then maximum amount of copolymerized MAN that could be achieved would be 2% of the number of normal end groups (if all of the MAN formed is incorporated). This amount would be essentially undetectable given the broadness of the envelope of signals due to the copolymerized MAN.

Another possible source of MAN is transfer to initiator. This process involves the propagating radical abstracting hydrogen from AIBN and the radical formed then undergoing β-scission to afford a cyanoisopropyl radical and a molecule of MAN (see below).[19]

The absolute number of end groups per molecule cannot be determined with great accuracy because of the cumulative errors associated with determining the degree of enrichment of the AIBN, the molecular weight of the polymer, and the integration of the spectrum. However, the systematic nature of many of the errors means that the relative number of end groups per molecule should be accurate to within ±10%. It is notable that low-conversion polymers (A and B) prepared with 0.01 and 0.2 M AIBN, respectively, have the same number of end groups per molecule.

However, the higher conversion polymers (C and D) appear to have approximately 20% more end groups per molecule than the polymerizations taken to only 8% conversion (A and B) (see Table I). A similar observation (>2 end groups per molecule at high conversion) was made by Henrici-Olive,[6] who determined the end groups of AIBN-initiated polystyrene by a radiochemical technique and suggested that the polymer may be branched (i.e., have three or more end groups per molecule). The mechanism for such branching is, however, uncertain. It was noted by Ayrey[28] that there is little precedent for cyanoisopropyl radicals being able to abstract hydrogen from the polystyrene backbone and thus initiate branching. On this basis he made the suggestion that the additional groups might arise by copolymerization of MAN formed during the reaction.[28] This explanation is ruled out by the present work. Studies aimed at verifying the trend for a higher number of end groups per molecule at higher conversions and at ascertaining the mechanism for the incorporation of any additional end groups in high-conversion polystyrene are currently in progress.

No signals which might be due to end groups from primary radical termination, expected to appear in the region 36–37 ppm, are observed in the ^{13}C NMR spectra of our polymers (we estimate that the lower limit of detectability for such groups would be 2% of total cyanoisopropyl end groups). This result is in conflict with some recent estimates of the importance of the process made by the analysis of polymerization kinetics.[3,5,22–25] It has been suggested that, under conditions similar to those used for the preparation of sample A, ca. 10%[3,22,24] or more of polymer chains are terminated by primary radical termination. It is significant that even in the oligomerization experiment (see above) which involved using a low styrene concentration and high rate of initiator decomposition, conditions which should favor primary radical termination, greater than 85% of chains are terminated by reaction between two oligostyryl radicals.

Our data also indicate that transfer to initiator does not occur by cyanoisopropyl group transfer, as has been suggested by some workers.[3,30] Moreover, transfer to initiator by hydrogen atom abstraction should lead to a decrease in the number of cyanoisopropyl residues per molecule and the production of a corresponding amount of MAN.[19] Thus, the observations that the polymers A and B have the same number of end groups per molecule and contain no copolymerized MAN, enable us to put an upper limit of 5% on the number of chains that are terminated by

transfer to initiator for low conversions and [AIBN] < 0.2 M. This limit, which corresponds to a transfer constant (C_I) of <0.01, suggests that the literature values of C_I (in the range 0.02–0.16)[3,20,22,25] are too high.

The polymer C which was prepared in bulk and carried to high (85%) conversion has a broad ($\bar{M}_w/\bar{M}_n \simeq 5.7$) bimodal molecular weight distribution due to the influence of the gel or Trommsdorf effect[31] and its NMR spectrum contains peaks attributable to copolymerized MAN. The level of copolymerized MAN in this sample is expected to be higher than in the low-conversion polymers for two reasons. First, the proportion of termination by chain-transfer reactions should be enhanced by the onset of the gel effect since the "normal" termination processes which involve reaction between polystyryl radicals are slowed through chain entanglement.[31] In addition, there is evidence to suggest that percentage of cyanoisopropyl radicals lost in the cage reaction (and hence the amount of MAN formed by this process) will be greater at high conversions (initiator efficiency will be lower) due to the increased viscosity of the reaction medium.[32] We are not in a position at this stage to comment on the relative importance of these two processes, although we can note, that all of the copolymerized MAN observed in polymer C could be accounted for if 10–15% of chains were terminated by transfer to initiator.

It is noteworthy that polymers prepared under similar conditions to those used for the preparation of sample C but using benzoyl peroxide as the initiator have a more normal molecular weight distribution ($\bar{M}_w/\bar{M}_n \simeq 1.8$).[8,33] This is attributed to the fact that when polymers are prepared with the latter initiator at high conversions most chains terminate by transfer to initiator or by primary radical termination.[33] On the basis of data given in our previous paper,[8] it is possible to calculate that, for a polymer prepared with 0.1 M benzoyl peroxide, between 30 and 80% conversion, greater than 75% of chains terminate by transfer to initiator or by primary radical termination.

In conclusion, the data presented in this and the previous paper[8] show that the properties of polystyrene will be dependent on the type and concentration of initiator used in its preparation. This is particularly true for high-conversion polymers prepared with AIBN and benzoyl peroxide[8] as the initiators. These polymers, as well as having different initiator-derived functionality, may have a very different molecular weight distribution and hence can be expected to show different physical properties.

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