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Poly(vinyl chloride) Structural Segments Derived from Azobis(isobutyronitrile)

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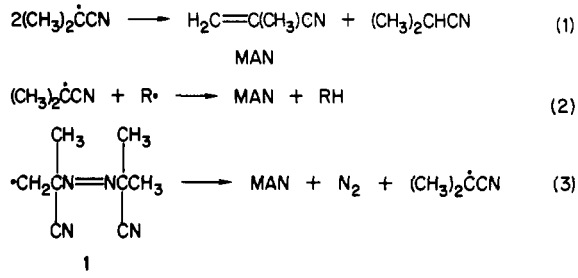
ABSTRACT: Poly(vinyl chloride) (PVC) prepared in 1,2-dichloroethane solution at 40 °C is shown to contain two types of nitrile structure derived from the polymerization initiator, azobis(isobutyronitrile) (AIBN). These structures have been identified by comparing the ^{13}C NMR spectra of their Bu_3SnH reduction products with those of appropriate models, whose synthesis is described. One of the nitrile moieties, an end group, results from the expected addition of the initiator radical, $(CH_3)_2\dot{C}CN$, to monomer, followed by conventional chain propagation. However, the other nitrile segment is internal and could only have been introduced by the copolymerization of vinyl chloride with methacrylonitrile (MAN). Kinetic analysis shows that the requisite amount of MAN could not have been formed in situ in all of the polymerizations that were studied, and that MAN must therefore have been present in the starting initiator at levels of $\leq 0.1_5$ wt %. The conclusive identification of MAN units in PVC reopens the question of the relative amounts of PVC chain termination by disproportionation and combination, as deduced from labeling studies with AIBN containing ^{14}C.

For many years azobis(isobutyronitrile) (AIBN) has been firmly entrenched in the role of a very popular initiator for free-radical polymerization. Its frequent use for this purpose has led to many detailed inspections of its thermolysis chemistry[1] and to its inclusion in numerous studies where mechanisms of polymerization have been addressed. For instance, ^{14}C-labeled AIBN and radiochemical assay have been used to determine the number of initiator fragments in poly(vinyl chloride)[2] (PVC) and, thus, to deduce the ratio of combination to disproportionation during the termination of PVC chains.[2a,c]

In the absence of contravening structural evidence, the assumption has been made frequently (e.g., for PVC)[2] that the AIBN moieties in polymers occur exclusively at chain ends. Nevertheless, it has long been recognized[3] that AIBN decomposition is a likely source of methacrylonitrile (MAN), whose free-radical polymerization and copolymerization are well-known. Hence, MAN units are conceivable "impurities" in all vinyl polymers that have been prepared using AIBN. This possibility was considered (but not confirmed) for poly(vinyl acetate) at least as early as 1955.[4]

There are several potential mechanisms for MAN formation during polymerization reactions, including (a) the disproportionation of carbon radicals derived from the AIBN (eq 1),[1a,3-5] (b) the disproportionation of one of these radicals with a polymeric radical, R· (eq 2),[5a] and (c) the decomposition (eq 3) of a radical (1) formed from AIBN by hydrogen abstraction.[6] Moreover, MAN may also be introduced into polymerizing systems as an impurity in



AIBN, since it is formed when the initiator is subjected to a standard method of purification (recrystallization from hot methanol).[8] However, several quantitative product studies have shown that AIBN thermolysis gives MAN in yields that are low at best, the major organic products being a ketenimine, $(CH_3)_2C{=}C{=}NC(CH_3)_2CN$, and tetramethylsuccinonitrile.[1,3,5,6a,9]

At present, the most convincing evidence for the occurrence of anomalous structures in polymers consists of NMR spectra in which the diagnostic resonances of such structures can be conclusively assigned. From ^{13}C NMR measurements, we have previously obtained such evidence for the presence of $(CH_3)_2C(CN)CH_2CH_2-$ chain ends in reductively dehalogenated PVC that had been polymerized with AIBN having a natural abundance of ^{13}C.[10] More recently, Bevington et al.[11] have also used ^{13}C spectra in order to identify similar end groups in a number of vinyl polymers. However, in their studies[11] the AIBN was enriched with ^{13}C, and not all of the unique resonances of the end groups were detected.

The present paper reports the details of earlier experiments[10] and of others relating to PVC which have shown that this polymer contains both terminal and internal segments arising from AIBN. These segments have been

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0024-9297/84/2217-2507$01.50/0

Table I
^{13}C Chemical Shifts of Nitrile Structures

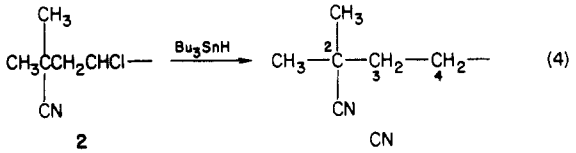
carbon	δ,[a] ppm (±0.05) vs. Me_4Si model[b]	reduced PVC
CN-CH_3	26.84	26.87
CH-CN	124.30	124.26
CN-2	32.49	32.40
CN-3	41.67	41.73
CN-4	25.53	25.50
CN′-CH_3	24.32	24.31
CN′-CN	123.85	123.82
CN′-br	37.02	36.99[c]
CN′-α	40.07	40.14
CN′-β	25.21	25.21

[a] At 110 °C in 4:1 (v/v) 1,2,4-trichlorobenzene/*p*-dioxane-d_8. [b] Data for compounds 4 and 6. [c] Tentative assignment.

identified by comparing the ^{13}C NMR spectra of Bu_3SnH-reduced PVC specimens with those of appropriate models containing the structures in question. Also discussed here are the kinetic aspects of the incorporation, into PVC, of the different fragments from AIBN.

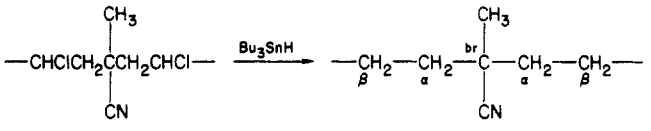
Results

The initiator end group (2) expected for AIBN-initiated PVC should be converted into a "CN" structure by reduction with Bu_3SnH (eq 4).



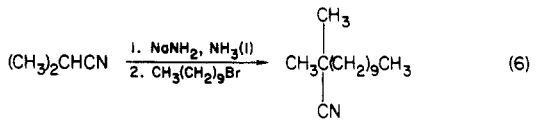
2 (4)

Similarly, the anticipated PVC segment (3) incorporating copolymerized MAN should be transformed upon reduction into the "CN′" arrangement (eq 5).

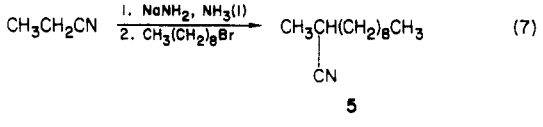


3 CN′ (5)

In the present investigation, a model (4) for the "CN" segment was obtained very conveniently by means of the simple alkylation reaction shown in eq 6,[10] while a "CN′"



(6)



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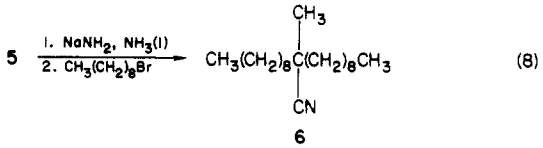

(8)

model, 6, was prepared in an analogous way (eq 7 and 8), via a nitrile intermediate (5) that was isolated and characterized. With the aid of appropriate comparative shift data,[12] the ^{13}C signals of these models were easily assigned, and several of them were found to be diagnostic of the "CN" and "CN′" structures. The chemical shifts of these

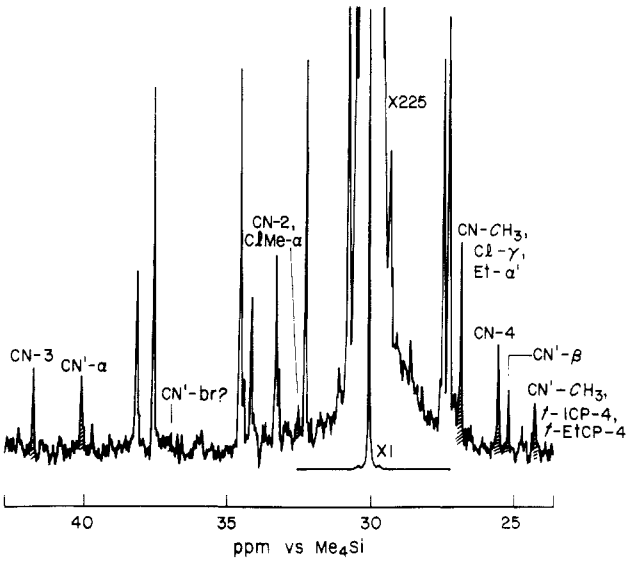

Figure 1. Proton-decoupled ^{13}C NMR partial spectrum (50.31 MHz) of a Bu_3SnH-reduced PVC specimen that had been polymerized at 40 °C in 1,2-dichloroethane with an average monomer concentration of 0.91 M and AIBN (0.027 M) as a thermal free-radical source. See text for nomenclature and discussion.

useful resonances are listed in the second column of Table I.

Figure 1 displays a partial ^{13}C spectrum of a Bu_3SnH-reduced sample of PVC that had been polymerized with initiation by unenriched AIBN. This spectrum contains conclusive evidence for the presence of both the "CN" and "CN′" structures, and their resonances are the only ones for which assignments are shown, the other important resonances having been identified in our earlier studies with similar specimens.[13]

The "CN-3", "CN-4", and "CN-CH_3" signals all appear at their correct positions in Figure 1, and with respective relative intensities of ca. 1:1:2, as required, even though the latter resonance is probably coincident with two others, "Cl-γ" and "Et-α'". These other resonances must thus be quite weak, and the spectrum supports this conclusion, in that it reveals concentrations of only ca. 0.1 and ≤0.2/(1000 C), respectively, for the "Cl" [$-(CH_2)_2CHCl(CH_2)_2-$] and "Et" [$-(CH_2)_2CH(CH_2CH_3)(CH_2)_2-$] structures (the "Cl" and "Et" ^{13}C shifts have been discussed in previous papers[13]). Observed as well is a "CN-2" signal whose intensity is relatively low, as one would expect for a carbon not bonded directly to protium.[14] In fact, the "CN-2" resonance is probably strengthened to some extent by an overlapping absorption of the $-(CH_2)_2CH(CH_2Cl)(CH_2)_2-$ arrangement (structure "ClMe"), for which a concentration of ~0.2/(1000 C) can be deduced with the aid of reference shift data.[15] On the other hand, the resonance of the unprotonated "CN-CN" carbon is too weak for detection in the downfield part of the spectrum that has been omitted from Figure 1. However, this resonance did appear in the spectrum of another reduced sample (see below) containing a higher "CN" concentration.

Figure 1 also displays distinct resonances for the "CN′-α", "CN′-β", and "CN′-CH_3" carbons. As predicted, the intensities of the "CN′-α" and "CN′-β" signals are roughly comparable, whereas the "CN′-CH_3" resonance is somewhat stronger than is required. This minor discrepancy can be ascribed to the presence of underlying resonances arising from trans internal cyclopentane[16] ("*t*-ICP") and *trans*-1-ethyl-2-(long alkyl)cyclopentane[17] ("*t*-EtCP") structures formed during the reduction process. With recourse to their ^{13}C shifts, which are known,[16,17] the total

Table II
Concentrations of Nitrile Structures in Bu_3SnH-Reduced PVC

	no. (±10%) per 1000 C	
$[VC]_m$,[a] M	CN	CN′
4.61	0.2	≤0.1[b]
0.91	1.0[c]	0.4[c]
0.46	2.1	0.1_5

[a] Mean monomer concentration during polymerization at 40 °C in 1,2-dichloroethane with initiation by 0.027 M AIBN. [b] Not detected. [c] Value calculated from the spectrum of Figure 1.

concentration of these cyclopentanes can be estimated to be about 0.1/(1000 C), a value that accounts satisfactorily for the "extra" "CN′-CH_3" signal intensity. The resonance of the quaternary "CN′-br" carbon would be very weak, of course,[14] and the evidence for its presence is not convincing. However, a clear-cut "CN′-*C*N" signal occurs downfield, although it has not been shown in the figure.

Table I reveals that the chemical shifts of the "CN" and "CN′" polymer resonances are identical with those of the models within the probable limits of error, and our identification of these resonances is also strongly supported by their absence from the spectra of all reduced samples of PVC that has not been polymerized with AIBN, as observed in our earlier studies.[13]

Table II contains the concentrations, as determined by ^{13}C NMR, of the nitrile structures in three specimens of the reductively dehalogenated polymer. These values were derived from the ratios of the "CN-4" and "CN′-β" peak heights to the height of the principal carbon absorption, on the assumption that the NOE factors were full (as found for polyethylene carbons under conditions similar to ours[18]), and that the results were not being affected appreciably by differences in T_1. Some polyethylene T_1 data[18,19] tend to confirm the latter assumption for the pulsing conditions that we used, but these data do not entirely rule out the possibility that our "CN" concentrations are somewhat too low. Nevertheless, the relative amounts of this structure, as deduced from our absolute values, should still be strictly correct, since all of our spectra were obtained and analyzed in an identical manner.

Discussion

When no end groups are introduced by primary radical termination involving the combination of initiator $(CH_3)_2\dot{C}CN$ radicals with growing-chain polymer radicals ("primary radical coupling"), then the experimental "CN" concentration, $[CN]_{ex}$, as determined by our method in units of $(1000\ C)^{-1}$, will be given by $500(R_i)_m/k_p[R\cdot]_m[VC]_m$, where R_i is the rate of initiation; the bracketed terms are molar concentrations; subscript m refers to mean values; and k_p is the rate constant for ordinary chain propagation via the addition of polymeric $-CH_2\dot{C}HCl$ radicals (R·) to vinyl chloride monomer (VC). Under steady-state conditions, $[R\cdot]_m$ can be replaced by $[(R_i)_m/2k_t]^{1/2}$, k_t being the termination rate constant, and this substitution yields eq 9. Since all of our polymerizations were carried out

$$[CN]_{ex} = 500[2k_t(R_i)_m]^{1/2}/k_p[VC]_m \quad (9)$$

for the same length of time and with the same initial concentration of AIBN, $(R_i)_m$ would have been identical for every case, *unless* the initiator efficiency (for free-radical production) had been a function of $[VC]_m$. Therefore, it follows from eq 9 that a plot of our $[CN]_{ex}$ values (Table II) vs. $[VC]_m^{-1}$ should be linear and extend through the origin. Both of these predictions are fulfilled within the error limits of our results. Thus the initiator efficiency appears to have been invariant, and there is no evidence here for primary radical coupling. However, a larger (and more accurate) data base would be needed, of course, for a rigorous proof of these statements. Also, it might be argued that when the monomer concentration is diminished, decreased initiator tending ending to decrease the "CN" concentration are accompanied by increasing amounts of primary radical coupling, which would tend to cause the "CN" content to rise.

From our $[CN]_{ex}$ values and the molecular-weight data in the Experimental Section, the number of initiator end groups per number-average polymer molecule can be calculated to be 0.17–0.20, 0.29, and 0.34–0.35 for the polymers made at $[VC]_m$'s of 4.61, 0.91, and 0.46 M, respectively. The trend revealed by these values can be predicted by theory[2c] and must result from the decreased rate of polymer molecule completion by transfer to monomer when the monomer concentration is lowered.

Turning now to the "CN′" concentrations, we note that the number of "CN′" structures per ordinary VC monomer unit will be equal to $k_p'[MAN]_m/k_p[VC]_m$, where k_p' is the rate constant for the addition of R· to MAN, and the other symbols are as previously defined. The experimental "CN′" concentration, per thousand carbons, will thus be given by eq 10. Now in view of the identical time of

$$[CN']_{ex} = 500k_p'[MAN]_m/k_p[VC]_m \quad (10)$$

reaction used for all of the polymerizations, the total amount of MAN formed in situ should have been at least as great for the 0.91 and 0.46 M $[VC]_m$ runs as for the polymerization at 4.61 M $[VC]_m$. In fact, the MAN yield conceivably could have increased with decreasing $[VC]_m$, owing to the attendant decreases in the rates of the radical reactions (additions to vinyl chloride) that would have competed with MAN formation via the mechanisms noted above. It follows, therefore, from eq 10 that $[CN']_{ex}$ should certainly have shown a steady increase as $[VC]_m$ was lowered. Yet Table II shows that $[CN']_{ex}$ actually exhibits a maximum at 0.91 M $[VC]_m$! Clearly some other factor needs to be taken into account, and we now address the question of what this factor is.

The change in the MAN concentration with time will be given by eq 11, where y is the fractional yield of MAN

$$d[MAN]/dt = yk_d[I] - k_p'[R\cdot][MAN] \quad (11)$$

from AIBN thermolysis; k_d is the rate constant for this thermolysis; and [I] is the concentration of AIBN. From reported values[20] of k_d, it is apparent that the rate of initiation should have remained essentially constant throughout our polymerizations, since only 1–2% of the AIBN should have decomposed therein. Thus the starting initiator concentration (subscript 0) can be used in place of [I], and [R·] can be replaced by a constant, C. With these substitutions, eq 11 becomes eq 12. Integration of

$$d[MAN]/dt = yk_d[I]_0 - Ck_p'[MAN] \quad (12)$$

this expression within limits produces eq 13, where t refers

$$[MAN]_t = \frac{1}{Ck_p'}\{yk_d[I]_0 - (yk_d[I]_0 - Ck_p'[MAN]_0)e^{-Ck_p't}\} \quad (13)$$

to the total reaction time. Next we introduce eq 14, which

$$[CN']_{ex}([VC]_0 - [VC]_t)/500 = [MAN]_0 + y[I]_0(1 - e^{-k_dt}) - [MAN]_t \quad (14)$$

states that the "CN′" *molar* concentration in the reaction mixture at time t is equal to the sum of the molar concentrations of the MAN present initially and the total MAN formed in situ in the time interval from 0 to t, less

the actual molar concentration of MAN when t is reached. Combining eq 13 and 14 in order to eliminate $[MAN]_t$, we obtain eq 15 [this equation and eq 16 (see below) can be

$$[CN']_{ex} = \frac{500}{([VC]_0 - [VC]_t)}\left\{\left([MAN]_0 - \frac{yk_d[I]_0}{Ck_p'}\right) \times (1 - e^{-Ck_p't}) + y[I]_0(1 - e^{-k_dt})\right\} \quad (15)$$

simplified slightly by replacing $(1 - e^{-k_dt})$ with k_dt, since k_dt is very small].

For our system, $[I]_0 = 0.027$ M; $t = 10$ h; and $[MAN]_0$ will, for the moment, be assumed to be nil. In order to evaluate Ck_p', we first obtain Ck_p from the integrated first-order rate law for VC disappearance ($[VC]_0/[VC]_t = e^{Ck_pt}$) and the initial and final VC concentrations during our three polymerizations. This exercise yields a value for Ck_p of $(18 \pm 1) \times 10^{-3}$ h^{-1}, where the deviation is the average from the mean. Now Ayrey et al.[11c] have shown recently that methyl methacrylate (MMA) is 20 times as reactive as VC toward the $-CH_2\dot{C}HCl$ radical at 45 °C, and the reactivity of MAN toward this radical can be estimated to be greater than that of MMA by a factor of about 1.6, on the reasonable assumption that the MAN/MMA reactivity ratio is the same as the acrylonitrile/(methyl acrylate) reactivity ratio toward $-CH_2\dot{C}HCl$ at comparable temperatures (the latter ratio can be approximated from published data[21]). Hence, in our system, k_p'/k_p should be about 32, and Ck_p' should thus be $\sim 32\ Ck_p$, or 0.58 ± 0.03 h^{-1}. Several independent studies[1a,5] have shown that y is ca. 0.05, whereas reported values for k_d at 40 °C range[20] from 7.75×10^{-4} h^{-1} (in CCl_4)[22] up to 2.2×10^{-3} h^{-1} (in chlorobenzene).[2c] However, even if the larger of these k_d's is used in eq 15, along with the other data just given, the resultant value of $[CN']_{ex}$ is found to be only 0.07/(1000 C) for the 0.91 M $[VC]_m$ polymer. This $[CN']_{ex}$ is less by a factor of 6 than the actual value in Table II, a very striking discrepancy that certainly seems large enough to be real. It can be removed, of course, by increasing y, either with or without an attendant increase in Ck_p'. However, if such an adjustment were made, eq 15 would then predict a $[CN']_{ex}$ value of 0.9/(1000 C) for the 0.46 M $[VC]_m$ specimen,[23] as compared to the measured value (in Table II) of only 0.1_5/(1000 C). We are therefore forced to conclude that the discrepancy found at 0.91 M $[VC]_m$ must be ascribed to *the presence of MAN as an impurity in the starting AIBN*. In fact, using the same numerical data as before, we find that eq 15 yields the correct value of $[CN']_{ex}$ when $[MAN]_0$ is 1×10^{-4} M. This concentration corresponds to an MAN level in the initiator of only 0.1_5 wt %, an amount that does not seem unreasonable for recrystallized AIBN.[24]

From eq 15 it follows that the same degree of contamination by MAN would have led to a $[CN']_{ex}$ value of only 0.09/(1000 C) for the polymer made at 4.61 M $[VC]_m$. Since this "CN′" content would have been below our detection limit by NMR, it is easy to see why the "CN′" structure was not identified in this sample. On the other hand, eq 15 predicts the correct value of $[CN']_{ex}$ for the 0.46 M $[VC]_m$ specimen when $[MAN]_0$ is zero. However, this result does not completely exclude the possibility of significant contamination by MAN in this polymerization, since the k_d value we have used thus far may actually be too large. If we use instead the lower k_d for CCl_4 solution[22] (7.75×10^{-4} h^{-1}), we find from eq 15 that $[MAN]_0$ must then be 1×10^{-4} M (as before) and $1_5 \times 10^{-6}$ M, respectively, for the 0.91 and 0.46 M $[VC]_m$ polymers. Both of these concentrations are greater than the total amount of MAN formed in situ when y is 0.05, and this statement also applies to the $[MAN]_0$ found above for the 0.91 M $[VC]_m$ sample when a k_d of 2.2×10^{-3} h^{-1} was used.

The smaller k_d was determined by radical scavenging with 2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazyl.[22] Thus this k_d may be too low,[25] and in fact there is evidence suggesting that the true k_d for our system lies between the two extremes. Assuming no termination by primary radical coupling (as implied by our results; see above) and an initiator efficiency, f, in the range of 0.4 to 0.6,[2c,25b,26] we can use k_d with eq 16 to predict $[CN]_{ex}$ for our polymers.

$$[CN]_{ex} = 10^3 f[I]_0(1 - e^{-k_dt})/([VC]_0 - [VC]_t) \quad (16)$$

When k_d is 2.2×10^{-3} h^{-1}, the predicted T_1's are 30–130% too high, but if k_d is only 7.75×10^{-4} h^{-1}, the predicted values are too low by some 20–50%. For an f of 0.5, a k_d of 1.3×10^{-3} h^{-1} predicts values of $[CN]_{ex}$ that agree well with our experimental figures, but obviously we cannot be certain that this k_d is precisely correct, since the initiator efficiency in our system is actually unknown, and our measured $[CN]_{ex}$ values may be a bit low, as was pointed out previously. Nevertheless, it is instructive to note that these values and the rate of initiation can be checked by using them in eq 9 in order to calculate the value of $k_p/k_t^{1/2}$. Equation 9 shows that $k_p/k_t^{1/2}$ can be obtained by dividing $500[2(R_i)_m]^{1/2}$ by the slope of the plot of $[CN]_{ex}$ vs. $[VC]_m^{-1}$, and if we use our experimental value of the slope (0.95 M) and take $(R_i)_m = 2fk_d[I]_0 = 2(0.5)(1.3 \times 10^{-3})(0.027) = 3.5 \times 10^{-5}$ M·h^{-1}, we find by this procedure that $k_p/k_t^{1/2}$ is 4.4 M$^{-1/2}$·h$^{-1/2}$. This value agrees satisfactorily with a reported value of 4.1 M$^{-1/2}$·h$^{-1/2}$ that was derived from kinetic measurements on the benzoyl peroxide-initiated polymerization of vinyl chloride in dichloroethane at 40 °C.[27] We conclude, therefore, that the errors in our $[CN]_{ex}$ and $(R_i)_m$ values are unlikely to be large.

Concluding Remarks

It now is quite apparent that copolymerized MAN units are likely to exist to some extent in any PVC specimen that has been polymerized with AIBN. These units may be present in other vinyl polymers, as well, and from the preceding discussion it follows that their introduction will be favored by a high concentration of AIBN, a low concentration of vinyl monomer, a relatively low reactivity of the monomer toward growing-chain polymer radicals, and, of course, the contamination of AIBN by MAN, which may be much more important than it has been thought to be heretofore.[28] Copolymerization with MAN is at least a potential source of significant error in any mechanistic investigation where all of the polymer-bound fragments from AIBN are required to be at the ends of chains.

Lastly, we note that our results do not necessarily invalidate the conclusions of the published studies[2] of PVC chain termination in the presence of ^{14}C-labeled AIBN. The reason is that we have no direct information about the MAN contents of the polymers on which these studies were based. Nevertheless, our findings do suggest that it might be desirable to reexamine this problem using ^{13}C NMR analysis and the procedure of Park and Smith,[2c] in order to minimize complications arising from transfer reactions.

Experimental Section

Materials. Vinyl chloride obtained from BP Chemicals or Matheson was dried with magnesium perchlorate, subjected to several cycles of freeze–pump–thaw degassing, and then distilled on a vacuum line, the middle third of the distillate being retained

for subsequent use. The AIBN was recrystallized carefully from absolute ethanol, and the 1,2-dichloroethane (Analytical Reagent grade) was used as received. All other starting materials, reagents, and solvents were either commercial products of very high purity or laboratory specimens that had been synthesized by conventional methods. Further purification, if necessary, was accomplished with standard techniques.

Instrumental Analysis. Pulse Fourier transform ^{13}C NMR spectra of the reduced polymer samples were recorded at 50.31 MHz with a Varian XL-200 instrument using a sweep width of 8000 Hz, 32K data points, a 90° pulse with a width of 13 μs, broadband proton decoupling, floating-point arithmetic, 1.000-Hz line broadening, a pulse repetition time of 10.0 s, 4:1 (v/v) 1,2,4-trichlorobenzene/*p*-dioxane-d_8 as solvent, hexamethyldisiloxane as an internal reference (2.00 ppm vs. Me_4Si), and a sample solution temperature of 110 °C. The spectrum of Figure 1 represents a total accumulation of 8400 transients from a solution having a sample concentration of 15.6% (w/v). Model-compound ^{13}C spectra also were obtained on the XL-200 spectrometer or at 22.49 MHz on a JEOL FX90Q Fourier transform instrument. The ^1H NMR measurements were made with a Varian T-60A spectrometer at ambient temperature; IR spectra were taken with a Perkin-Elmer instrument, Model 597. Programmed-temperature gas chromatography (GC) analyses were performed with a Varian 3700 instrument using flame-ionization detection and 6-ft × 0.125-in. (o.d.) stainless steel columns containing (a) 5% of FFAP on 100–120 mesh Chromosorb-W or (b) 10% of OV-101 on 80–100 mesh Chromosorb-WHP. Preparative high-performance liquid chromatography (HPLC) was carried out with a Waters Prep 500A chromatograph using a Waters PrepPAK-500/SILICA cartridge and hexane as the eluant. Molecular weights of the PVC samples were obtained by the Rubber and Plastics Research Association of Great Britain (RAPRA) via gel permeation chromatography (GPC); those of the reduced polymers were determined by GPC at AT&T Bell Laboratories, according to a rigorously tested procedure involving the use of linear polyethylene fractions as standards.

PVC Preparation. Polymerizations were carried out at 40 ± 0.1 °C in evacuated ampules containing freeze–pump–thaw degassed solutions of vinyl chloride (initial concentration: 5.00, 1.00, or 0.50 M) and AIBN (0.027 M) in 1,2-dichloroethane. Polymer precipitation did not occur in any of the polymerization runs. The polymer samples were isolated by precipitation into methanol and then purified by repeated dissolution in tetrahydrofuran (THF) and reprecipitation with methanol, followed by drying at room temperature under vacuum. Average monomer concentrations were calculated from conversion percentages derived from the yields of purified polymer. Molecular-weight measurements gave the following results for the PVC samples thus obtained (average monomer concentration, $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_w/\bar{M}_n$, number-average degree of polymerization): 4.61 M, 26 740, 63 340, 2.37, 428; 0.91 M, 9067, 17 800, 1.96, 145; 0.46 M, 5128, 8465, 1.65, 82.

PVC Reduction. The reductions were done with Bu_3SnH via a "two-pass" procedure that was identical with a published method[29] in all significant respects, except for the use of THF as the solvent[13] in the first reduction stage. The reduced samples were purified by dissolution in hot xylene, precipitation with methanol, and subsequent drying at room temperature under vacuum. Molecular-weight measurements on two of these specimens yielded the following results (average monomer concentration during polymerization, $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_w/\bar{M}_n$, number-average degree of polymerization): 4.61 M, 13 780, 32 850, 2.38, 491; 0.46 M, 2360, 4650, 1.97, 84.

General Synthetic Procedures. The synthetic operations described below were carried out under dry nitrogen. Organic solutions were concentrated under low vacuum on a rotary evaporator; boiling points are uncorrected.

Preparation of 2,2-Dimethyl-*n*-dodecanonitrile (4). Isobutyronitrile (7.00 g, 0.101 mol) was added dropwise during 5 min to a stirred solution of sodium amide (4.48 g, 0.115 mol) in liquid ammonia (ca. 60 mL) at −68 °C. After an additional 10 min of stirring at −68 °C, a solution of 1-bromo-*n*-decane (25.4 g, 0.115 mol) in dry toluene (50 mL) was introduced dropwise during 15 min with continued stirring while the temperature was kept between −59 and −68 °C. Cooling was discontinued, and the ammonia was allowed to evaporate while the volume of the mixture was maintained by the introduction of additional anhydrous toluene. The mixture was then heated under reflux with stirring for 2 h, allowed to cool to room temperature, and filtered with suction in order to remove the precipitated solid, which was washed while on the filter with several fresh portions of dry toluene. Concentration of the combined filtrate and washings, followed by fractional distillation of the residue through an 80-plate spinning-band column, afforded 16.66 g (79%) of **4** (99.8% pure by GC analysis on column a): bp 117 °C (1.5 torr); IR (neat) 2230 cm^{-1} (CN stretch); ^1H NMR (CCl_4) δ 0.88 (distorted t, $J \simeq$ 6 Hz, 3, CH_3CH_2), 1.2–1.4 [m, 18, $(CH_2)_9$], and 1.4–1.5 [broad s, 6, $(CH_3)_2C(CN)$] ppm vs. Me_4Si; ^{13}C NMR [4:1 (v/v) 1,2,4-trichlorobenzene/*p*-dioxane-d_8, 110 °C] δ 124.30 (CN); 32.49 (C-2); 26.84 (gem CH_3's); 41.67 (C-3); 25.53 (C-4); 29.70, 29.85 (2 C's), and 30.03 (C-5, -6 -7, and -8; exact assignments uncertain); 29.55 (C-9); 32.19 (C-10); 22.89 (C-11); and 14.06 (C-12) ppm vs. Me_4Si.

Preparation of 2-Methyl-2-*n*-nonyl-*n*-undecanonitrile (6). Using a procedure which was similar to that adopted for the synthesis of **4**, propionitrile (5.56 g, 0.101 mol) was subjected to monoalkylation by 1-bromo-*n*-nonane (23.85 g, 0.115 mol) in liquid ammonia (~60 mL) containing sodium amide (4.48 g, 0.115 mol). After 5 h of stirring at ≤−60 °C, the mixture was allowed to warm to room temperature overnight, diluted with pentane, and filtered with suction. The solid was washed thoroughly on the filter with fresh pentane, and the filtrate and washings were combined, concentrated, and subjected to short-path distillation in order to obtain 9.63 g (53%) of **5** (98.7% pure by GC analysis on column b): bp 91–95 °C (0.5 torr); IR (neat) 2240 cm^{-1} (CN stretch); ^1H NMR (CCl_4) δ 0.88 (distorted t, $J \simeq$ 6 Hz, 3, CH_3CH_2), 1.1–1.7 [m, 19, $(CH_2)_8$ and $CH_3CH(CN)$], and 2.3–2.8 [m, 1, CH(CN)] ppm vs. Me_4Si. A further alkylation was performed in an analogous way by using 9.46 g (0.0522 mol) of **5**, 11.71 g (0.0565 mol) of 1-bromo-*n*-nonane, and 2.22 g (0.0569 mol) of sodium amide in ca. 60 mL of liquid ammonia. Following the usual workup, most of the unchanged **5** and bromononane were removed by short-path distillation, and the resultant semisolid residue was filtered with suction. Fractionation of the filtrate by preparative HPLC gave 0.93 g of nitrile **6** containing no detectable impurities: IR (neat) 2240 cm^{-1} (CN stretch); ^1H NMR (CCl_4) δ 0.90 (distorted t, $J \simeq$ 6 Hz, 6, 2 CH_3CH_2) and 1.1–1.6 [m, 35, 2 $(CH_2)_8$ and $CH_3C(CN)$] ppm vs. Me_4Si; ^{13}C NMR [4:1 (v/v) 1,2,4-trichlorobenzene/*p*-dioxane-d_8, 110 °C] δ 123.85 (CN); 37.02 (C-2); 40.07 (C-3); 25.21 (C-4); 29.78, 29.87, and 30.19 (C-5, -6, and -7; exact assignments uncertain); 29.59 (C-8); 32.23 (C-9); 22.91 (C-10); 14.05 (C-11); and 24.32 [$CH_3C(CN)$] ppm vs. Me_4Si. Spectral data and GC retention-time comparisons on column b showed that the 3.18 g of solid that had been removed from the distillation residue by filtration was **6** in a purity of ca. 90% (as determined from the GC analysis); hence the total crude yield of the desired nitrile was 4.11 g, or 26%, based on the starting amount of **5**.

Acknowledgment. We thank M. Y. Hellman for GPC molecular-weight data on reduced samples of PVC and the polymer supply and characterization services of RAPRA for GPC measurements on the unreduced polymers.

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Mechanism of Graft Copolymerization onto Polysaccharides Initiated by Metal Ion Oxidation Reactions of Model Compounds for Starch and Cellulose

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ABSTRACT: Oxidation of model compounds for starch and cellulose with Mn(III), Ce(IV), and V(V) ions has been studied by means of UV-vis absorption spectroscopy and ESR. The oxidation of diols proceeds via a stable complex and is almost first order with respect to proton concentration. Acyl radical spin adducts are detected as intermediates from aldehydes and diols by means of ESR trapping experiments. Reactivity studies reveal that cis-C1–C2 glycol groups are oxidized 4 times faster than cis-C3–C4 glycol groups. Trans glycol groups and C6 hydroxyl groups have negligible reactivities. Model compounds for reducing end groups of polysaccharides are oxidized 50 times faster than model compounds for nonreducing end groups. Considering the large number of repeating diol groups along the polysaccharide chain, it is concluded that both C1–C2 (end groups) and C2–C3 glycol groups are predominant sites for initiation of graft copolymerization.

Introduction

Oxidation of alcohol and glycol groups involving free radicals has been used to develop a technique of graft copolymerization onto starch and cellulose. The most widely used system is that initiated by ceric ions, in which high grafting efficiencies have been obtained with both hydrophobic and hydrophilic monomers.[1-6]

On the basis of studies of model compounds, the initiation is thought to involve the formation of a complex between the metal ion and hydroxyl groups in the polysaccharide followed by disproportionation of the complex to generate radicals. The formation of radicals in cellulose

0024-9297/84/2217-2512$01.50/0