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Studies on the Radical Polymerization of Vinyl Acetate in Benzene, Chlorobenzene and Ethyl Acetate by ^{1}H NMR Spectroscopy

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Summary

Polymerizations of vinyl acetate were carried out with AIBN in benzene, chlorobenzene and ethyl acetate, and the resultant polymers were analyzed for terminal group by using ^{1}H NMR technique. The results revealed that a part of the polymer molecules prepared in aromatic solvent contained one solvent fragment at the chain end, indicating the incorporation of aromatic molecule through the chain transfer reaction and not by the copolymerization. It was found that there existed at least 0.7 branching per a molecule in the polymer prepared in ethyl acetate, whereas almost no branching in the polymer prepared in aromatic solvents.

Introduction

It is known for long that vinyl acetate polymerizes more rapidly in ethyl acetate than in aromatic solvent such as benzene (BURNETT and MELVILLE 1947), however, the true meaning of this phenomenon was not completely understood. Recently Kamachi and his coworkers (KAMACHI et al. 1979a; KAMACHI et al. 1979b) found the marked effect of solvent on the rate constants of radical polymerizations of vinyl acetate and attributed the slower rates of polymerization in aromatic solvents to the complex formation between the propagating radical and the π-electron system of solvent molecule. It was also suggested for this problem that the benzene molecule copolymerized with vinyl acetate, which caused a decrease in the apparent rate of polymerization (STOCKMAYER and PEEBLES, Jr. 1953; PEEBLES, Jr. et al. 1960).

In this work the polymerizations of vinyl acetate were carried out with AIBN in benzene, chlorobenzene and ethyl acetate, and the resultant polymers were analyzed for terminal group by using ^{1}H NMR technique. The results revealed that the polymer prepared in aromatic solvent contained the solvent fragment but the number of phenyl group in a polymer molecule was much less than unity, and it located at the end of the polymer

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chain. These strongly indicate that the aromatic solvent molecule was incorporated into the chain through the chain transfer reaction not by the copolymerization. The polymer prepared in ethyl acetate was also studied and the mechanisms of chain transfer and termination reactions in these three solvents were discussed in some detail.

Experimental

Vinyl acetate was polymerized with 2,2'-azoisobutyronitrile (AIBN) at 60°C. After a given polymerization time the reaction mixture was poured into a large amount of petroleum benzine and the precipitated polymer was collected by filtration, washed several times with petroleum benzine and dried in vacuo at room temperature. The polymer thus obtained was purified three times by reprecipitation in hexane from the dioxane solution. The resulting polymer was dissolved again in dioxane and freeze-dried. The results of the polymerizations were summarized in Table 1.

TABLE 1
Polymerizations of vinyl acetate with AIBN in several solvents at 60°C

Solvent	Time (hr)	Polymer	
		Yield(%)	$\bar{M}_n$[b]
benzene	20	54	15700
chlorobenzene	24	49	12100
ethyl acetate	2	47	23900

[a] Monomer 20mmol, AIBN 0.20mmol, solvent 8.13ml.
[b] Number average molecular weight was measured in toluene at 60°C by a Hitachi 117 vapor pressure osmometer.

The ^1H NMR spectra of the polymer were taken at 60°C in dimethyl sulfoxide-d_6 (DMSO-d_6) on JNM-FX100 and Bruker WM-360 Fourier transform NMR spectrometers at 100 and 360MHz, respectively. The concentration of the sample solution was about 30 wt/vol%. The chemical shifts were referred to the central peak of the multiplet resonance due to the remaining protons in the solvent DMSO-d_6 and converted into the shifts on TMS scale (DMSO - TMS = 2.50ppm). The free induction decays were accumulated 500 to 4000 times, and the 45° pulse and the repetition time of 10 sec were used. Spin-lattice relaxation time, T_1, was measured by the inversion-recovery Fourier transform method at 100MHz.

Results and Discussion

In Figure 1 are shown the 100MHz ^1H NMR spectra of poly(vinyl acetate) prepared in benzene with AIBN at 60°C. The results of analysis are given in Table 2. The assignments for the resonances due to the protons

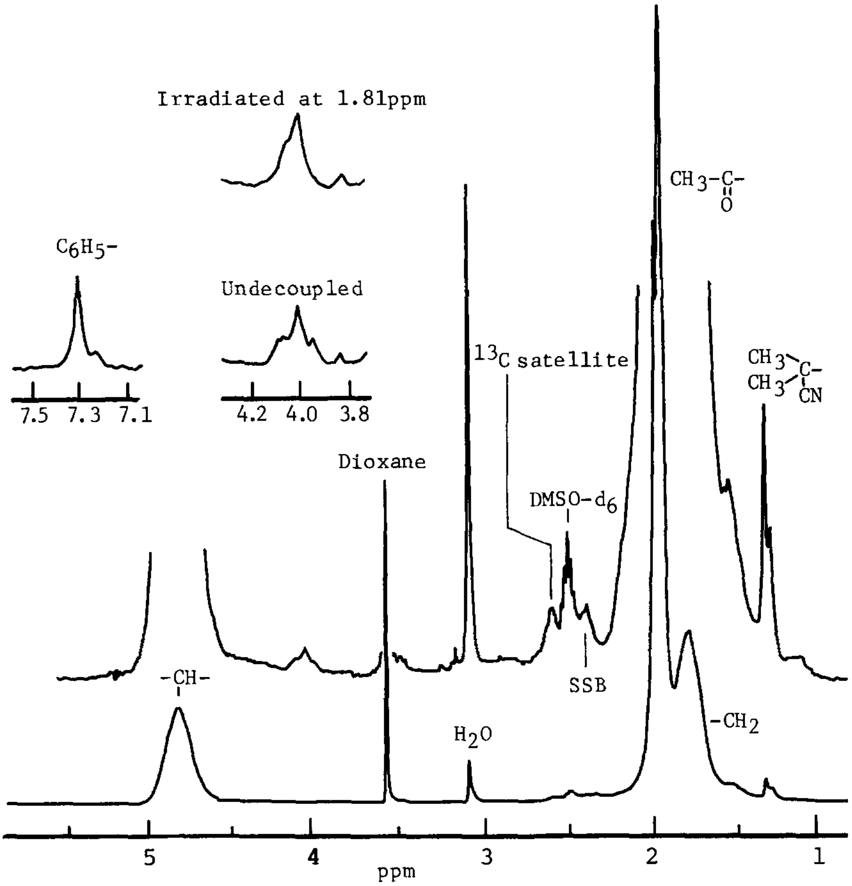
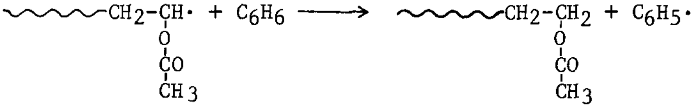
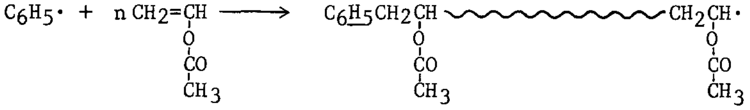


Figure 1 100MHz ^1H NMR spectra of poly(vinyl acetate) prepared in benzene with AIBN at 60°C (Measured in DMSO-d_6 at 60°C)

of the backbone methylene and methine groups and the acetoxy methyl group are indicated in the Figure. In the phenyl proton region a small but distinguishable signal was observed at 7.31ppm. This signal disappeared when the polymer was prepared in perdeuterated benzene. The ^1H spin-lattice relaxation time, T_1, for the peak was found to be 0.72 sec and much longer than those of the protons in the monomer unit in the polymer chain (0.09 sec for backbone methylene, 0.20 sec for backbone methine and 0.32 sec for acetoxy methyl). But it was the same order of magnitude as the T_1 of the phenyl proton in the toluene fragment located at the chain end of poly(styrene-d_8) (0.96 sec) (HATADA et al. unpublished). These clearly indicate that the signal at 7.31ppm is attributed to the protons of the phenyl group which was introduced at the chain end through the chain transfer reaction.



$$\sim\sim\sim CH_2-\underset{\substack{| \\ O \\ | \\ CO \\ | \\ CH_3}}{CH}\cdot + C_6H_6 \longrightarrow \sim\sim\sim CH_2-\underset{\substack{| \\ O \\ | \\ CO \\ | \\ CH_3}}{CH_2} + C_6H_5\cdot \qquad (1)$$



$$C_6H_5\cdot + n\,CH_2=\underset{\substack{| \\ O \\ | \\ CO \\ | \\ CH_3}}{CH} \longrightarrow C_6\underline{H}_5CH_2\underset{\substack{| \\ O \\ | \\ CO \\ | \\ CH_3}}{CH} \sim\sim\sim\sim\sim\sim CH_2\underset{\substack{| \\ O \\ | \\ CO \\ | \\ CH_3}}{CH}\cdot \qquad (2)$$

Direct measurement of the relative intensity of this phenyl proton signal to the signals of the monomer units in the chain was difficult owing to its lower intensity. So the intensity ratio of the phenyl signal to the singlet signal* at 3.1ppm was determined first to be 0.0875, and then the ratio of the latter signal to the backbone methine signal to be 0.048. Consequently, the ratio of the phenyl signal to the methine signal was found to be 0.0042. Calculation from this value and the molecular weight of the polymer showed that only 15% of the polymer chains contained one phenyl group at the chain end. The possibility of the copolymerization of benzene molecule was thus neglected. When the polymerization was carried out in chlorobenzene, the content of the aromatic group at the chain end (0.28 per a polymer molecule) was about twice as that in the polymer prepared in benzene (0.15) as shown in Table 2. This almost corresponds to the fact that the ratio of the chain transfer constants of chlorobenzene and benzene is 2.82 (PALIT and DAS 1954), indicating the validity of the incorporation of aromatic molecule through the chain transfer reaction.

TABLE 2
Analysis of the terminal group in the poly(vinyl acetate) prepared with AIBN at 60°C in benzene, chlorobenzene and ethyl acetate

Solvent	Terminal group (mol/mol[a])		
	AIBN	solvent	$CH_3COOC\underline{H}_2CH_2-$
benzene	1.24	0.15	0.56
chlorobenzene	1.20	0.28	0.41
ethyl acetate	0.42	more than 0.43	1.24

[a] Represents the number of terminal group per a polymer molecule.

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* This resonance was ascribed to a small amount of water incidentally introduced into the sample solution and its intensity was usually intermediate between those of the end group signal and the backbone methine one. The signal was not so sharp and not so broad as to be most appropriate to the standard for the intensity measurement

In the spectrum in Figure 1 there appeared a small triplet at 4.02ppm. The triplet turned out to a singlet by the irradiation at 1.81ppm where the backbone methylene proton resonated. Morishima et al. reported that the β-methylene protons of the β-acetoxyethyl group occuring as a short branching or a main-chain end group in the acetylated poly(vinyl alcohol) resonated at 4.08 ppm in $CDCl_3$ solution (MORISHIMA et al. 1975; MORISHIMA and NOZAKURA 1976). Then, the resonance at 4.02ppm should be ascribed to the methylene protons of the β-acetoxyethyl group ($CH_3COO\underline{CH_2}CH_2$-) which was formed at the chain end by the chain transfer reaction to benzene (reaction (1)-(2)). The amount of the β-acetoxyethyl group was determined to be 0.56 per a polymer molecule from the intensity measurement of the signal (Table 2). The content of the group due to the transfer to benzene should be 0.15. So the residual amount may be ascribed to the acetoxyethyl group which was formed through the chain transfer reaction to the monomer or polymer, backbiting of the growing radical or the termination reaction by disproportionation.

The peak at 1.31ppm* was mainly due to the methyl protons of the AIBN fragment, 1-cyano-1-methylethyl group, attached to the polymer chain, but overlapped with the ^{13}C satellite of the backbone methylene signal. The peak area of the another satellite at 2.60ppm was therefore substracted from the total area of the peak at 1.31ppm to correct for this overlap. Then the number of initiator fragments per a polymer molecule was calculated to be 1.24 for the polymer prepared in benzene and 1.20 for the polymer obtained in chlorobenzene (Table 2). This may be the first finding of an important contribution of combination reaction in the termination process in the polymerization of vinyl acetate.

In Figure 2 are shown the 360MHz ^1H NMR spectra of poly(vinyl acetate) prepared in ethyl acetate with AIBN. The resonance around 1.17ppm was composed of a triplet and doublet as shown in the Figure**, and assigned to the protons of the two types of methyl groups in the ethyl acetate fragments. These methyl groups would be incorporated into the polymer chain through the chain transfer reactions (3)-(4) and (5)-(6) and hydrogen abstraction of terminal radical formed by the head-to-head addition (7) (ADELMAN and FERGUSON 1975). The triplet turned out a singlet when irradiated around 4.05ppm. On the other hand, the doublet was changed into a singlet by the irradiation at 4.8ppm where the backbone methine proton resonated. The results are the

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* This peak almost disappeared when the polymer was prepared with diisopropyl peroxydicarbonate, whose fragment, isopropoxy group, showed a doublet at 1.23ppm

** Small peaks at 1.10, 1.12, 1.14 and 1.18ppm can not be assigned at present clear indication that the triplet is due to the methyl protons of the ethoxycarbonylmethyl group ($CH_3CH_2OCOCH_2$-) caused by the reaction (3)-(4) and the doublet due to the methyl group by the reactions (5)-(6) and (7). A small triplet at 2.29ppm should be assigned to the protons of the methylene group adjacent to the carbonyl carbon in the ethoxycarbonylmethyl group

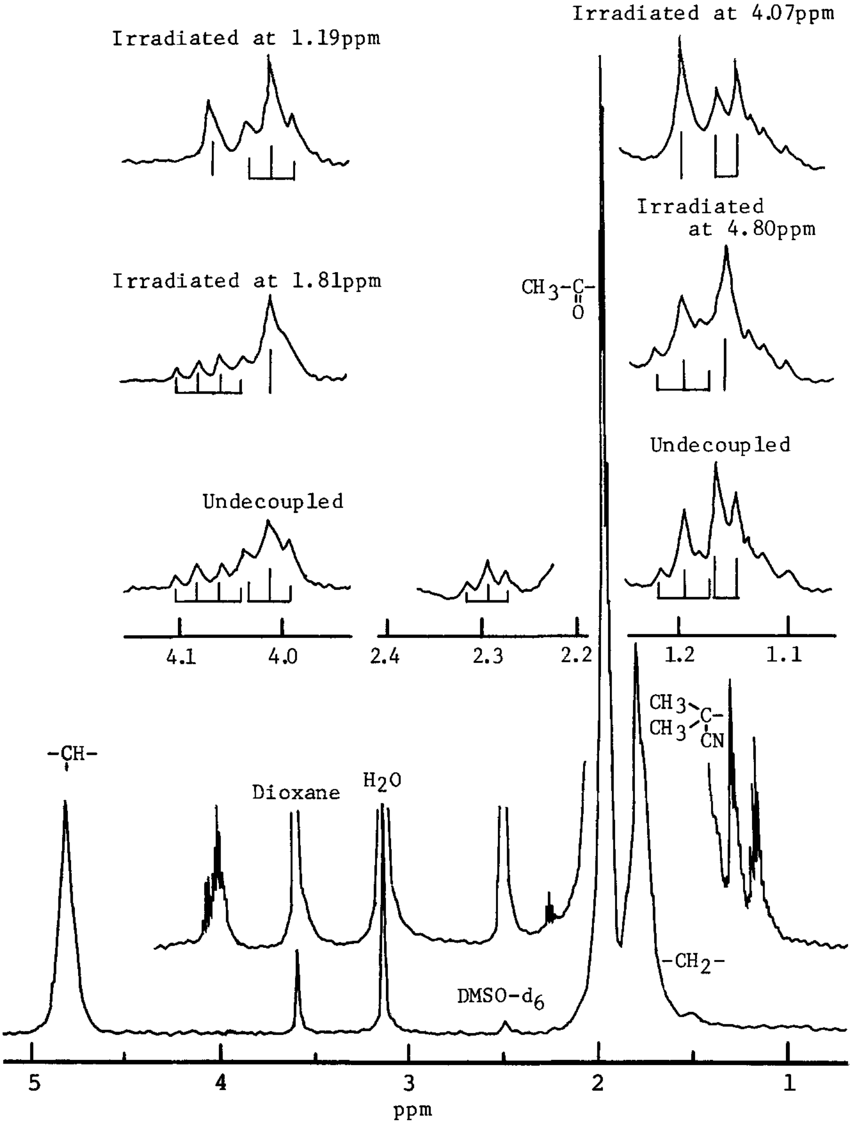
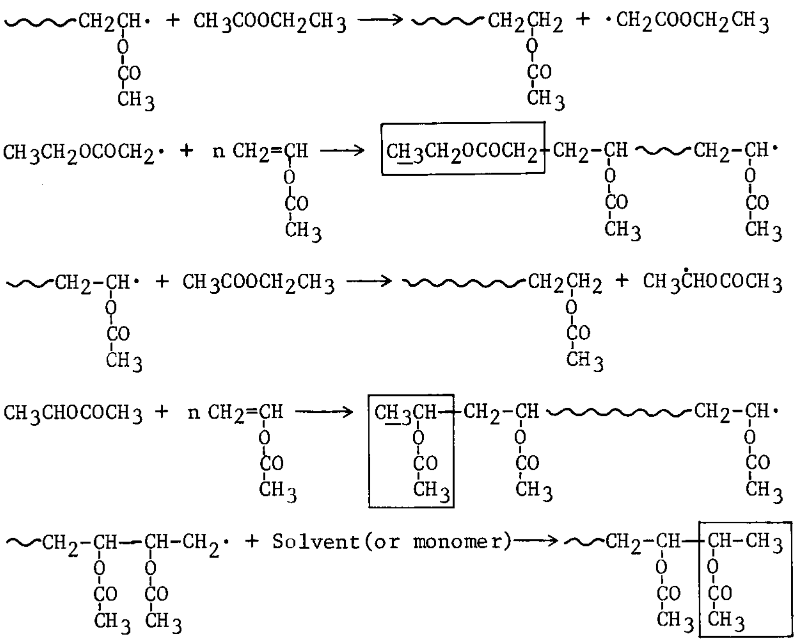


Figure 2 360MHz ^1H NMR spectrum of poly(vinyl acetate) prepared in ethyl acetate with AIBN at 60°C (in DMSO-d_6 at 60°C)



$$\sim\sim CH_2CH(OCOCH_3)\cdot + CH_3COOCH_2CH_3 \longrightarrow \sim\sim CH_2CH_2(OCOCH_3) + \cdot CH_2COOCH_2CH_3 \quad (3)$$

$$CH_3CH_2OCOCH_2\cdot + n\,CH_2{=}CH(OCOCH_3) \longrightarrow \boxed{C\underline{H}_3CH_2OCOCH_2}{-}CH_2{-}CH(OCOCH_3)\sim\sim CH_2{-}CH(OCOCH_3)\cdot \quad (4)$$

$$\sim\sim CH_2{-}CH(OCOCH_3)\cdot + CH_3COOCH_2CH_3 \longrightarrow \sim\sim CH_2CH_2(OCOCH_3) + CH_3\dot{C}HOCOCH_3 \quad (5)$$

$$CH_3CHOCOCH_3 + n\,CH_2{=}CH(OCOCH_3) \longrightarrow \boxed{C\underline{H}_3CH(OCOCH_3)}{-}CH_2{-}CH(OCOCH_3)\sim\sim CH_2{-}CH(OCOCH_3)\cdot \quad (6)$$

$$\sim CH_2{-}CH(OCOCH_3){-}CH(OCOCH_3){-}CH_2\cdot + \text{Solvent(or monomer)} \longrightarrow \sim CH_2{-}CH(OCOCH_3){-}\boxed{CH(OCOCH_3){-}CH_3} \quad (7)$$

($CH_3CH_2OCOC\underline{H_2}CH_2-$). The proportion of the triplet to doublet around 1.17ppm was 4 : 6 in their intensity. The total content of these methyl groups was measured to be 1.07 per a polymer molecule. Then the content of methyl group formed by solvent transfer reaction should be at least 0.43 (=1.07 × 0.4) per a polymer molecule indicating a higher extent of the chain transfer reaction to ethyl acetate than to aromatic solvent (Table 2).

From the spin-decoupling experiment mentioned above it is clear that the multiplet signal at 4.05ppm should include the quartet due to the methylene protons of the ethoxycarbonylmethyl group ($CH_3C\underline{H_2}OCOCH_2-$) introduced into the chain through the reaction (3)-(4). The multiplet came to the superposition of a singlet and a triplet by the irradiation at 1.19ppm. This indicates that the resonance at 4.05ppm is the overlap of a quartet and triplet and the latter should be due to the methylene protons of β-acetoxyethyl group ($CH_3COOC\underline{H_2}CH_2-$) which was formed at the chain end through the transfer reactions to solvent, monomer or polymer, and backbiting reaction of growing radical. The number of this group was calculated to be 1.24 per a polymer molecule from the intensity of the triplet. When decoupled from the backbone methylene protons (1.81ppm), the multiplet turned out to the overlap of a singlet and a quartet, and the latter was the two thirds of the triplet at 1.19ppm in the intensity. This is an additional evidence of the above assignment.

The number of the initiator fragments was determined to be 0.42 from the signal at 1.31ppm. Then the sum of the terminal groups amounted to 2.73(=0.42 + 1.07 + 1.24) per a polymer molecule, (cf. Table 2), indicating that the polymer prepared in ethyl acetate have at least 0.7 branching per a molecule. On the other hand, the sum totals of the terminal groups were 1.95 and 1.89, for the polymers prepared in benzene and chlorobenzene, respectively, indicating that there existed almost no branching in the polymer chain. The absence of branching may be due to the stabilization of the propagating radicals through the complex formation with aromatic solvent molecules.

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