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Studies on the Cationic Polymerization of Styrene by Using Perdeuterated Monomer

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Summary

Perdeuterated styrene was polymerized by $TiCl_4$ and $EtAlCl_2$ in toluene at -78°C and the resultant polymer was examined for the terminal group containg protons by using ^1H NMR spectroscopy. The polymer prepared by $TiCl_4$ was found to contain 0.64 of toluene fragments per a polymer molecule and a similar amount of CHD_2-group. The ratios of k_M/kp and k_S/kp were estimated to be 0.0228 and 0.0035, respectively. Similar results were obtained for the polymerization initiated with $EtAlCl_2$

Introduction

The reaction mechanism of anionic polymerization of methyl methacrylate has been studied by using perdeuterated monomer (HATADA et al. 1978). In this work perdeuterated styrene was polymerized by titanium tetrachloride($TiCl_4$) and ethylaluminum dichloride($EtAlCl_2$) in toluene and the resultant polymer was examined for the terminal group containing protons by using ^1H NMR spectroscopy to investigate the initiation and chain transfer reaction.

Experimental

Perdeuterated styrene was obtained from Aldrich Chemical Co., Inc. and purified by the distillation over calcium hydride under reduced nitrogen pressure.

Polymerization was carried out in toluene at -78°C and was terminated by the addition of a small amount of methanol. The reaction mixture was poured into a large amount of methanol, and the precipitated polymer was collected by filtration, washed with methanol and dried in vacuo at 50°C. The results are shown in Table 1.

^1H NMR spectra of the polymer were measured in nitrobenzene-d_5 at 110°C and 100MHz on JNM-FX100 Fourier transform NMR spectrometer (JEOL). The free induction decays were accumulated 200 times. Hydrogen contents of the sample were determined from the relative intensity of the signal of interest to the signal due to the remaining protons in the nitrobenzene-d_5 used as a

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TABLE 1
Polymerization of perdeuterated styrene in toluene at -78°C for 24hr[a]

Initiator	Yield (g)	Yield (mmol)	$\bar{M}_n \times 10^{-3}$
$TiCl_4$	0.148	0.0835	1.77
$EtAlCl_2$	0.154	0.0772	2.00

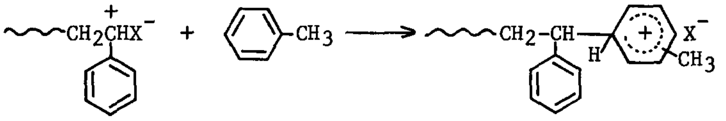
[a] Monomer 4.02 mmol, initiator 0.20 mmol, toluene 5ml.

solvent. The absolute intensity of the latter signal was measured by using precision coaxial tubing method (HATADA et al. 1977). Spin-lattice relaxation time, T_1, was measured by the inversion-recovery method.

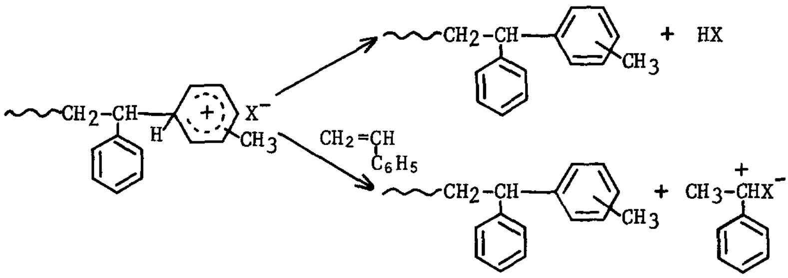
Number average molecular weight was determined in benzene by Hitachi 117 vapor pressure osmometer at 42°C.

Results and Discussion

In the cationic polymerization of styrene in aromatic solvent, such as toluene, the polymer contained a solvent fragment incorporated by the chain transfer reaction to a solvent molecule (PLESCH 1953; OVERBERGER and ENDRES, 1955; OVERBERGER et al. 1956; HIGASHIMURA et al. 1956).



(1)



(2)

(3)

In Figure 1 is shown the ^1H NMR spectrum of the polymer prepared in toluene at -78°C by $TiCl_4$. The polymer prepared by $EtAlCl_2$ showed a similar spectrum. There appear three signals at 6.92, 2.15 and 0.97ppm, whose spin-lattice relaxation times were 2.1, 0.89 and 4.6 sec., respectively. From the chemical shift consideration the first two peaks could be assigned to the phenyl and methyl protons of the toluene fragments incorporated into the polymer chain. The values of the relaxation times indicate that these two peaks did not come from the protons of the toluene molecules as contaminant. The intensity of the phenyl proton resonance showed that the polymers prepared by $TiCl_4$ and $EtAlCl_2$ contained 0.64 and 0.71 of toluene fragments per a polymer molecule, respectively (Table 2). The

TABLE 2
^1H NMR analyses of the polymers

Initiator	Toluene fragments				CHD_2-	
	Methyl		Phenyl			
	mmol	(mol/mol)[a]	mmol	(mol/mol)[a]	mmol	(mol/mol)[a]
$TiCl_4$	0.0533	0.64	0.0535	0.64	0.0594	0.71
$EtAlCl_2$	0.0545	0.71	0.0545	0.71	0.0608	0.79

[a] Represents the number of fragments per a polymer molecule.

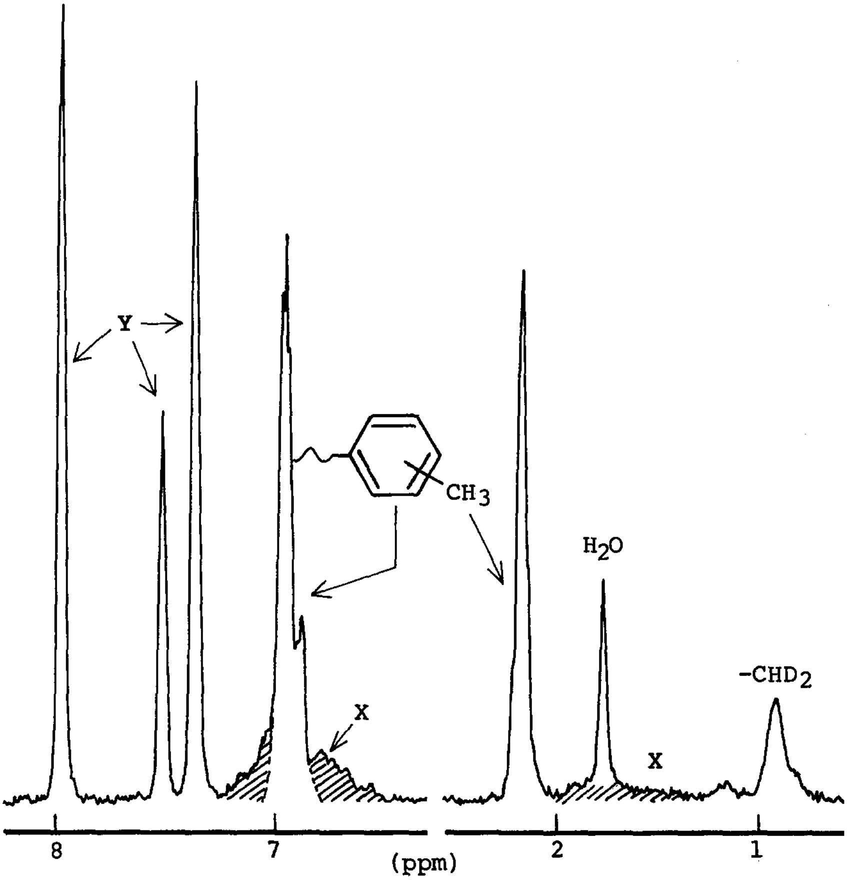
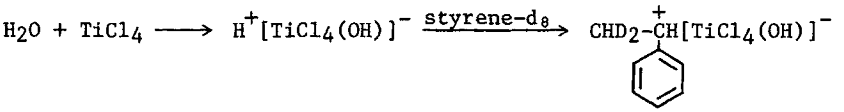


Fig. 1 ^1H NMR spectrum of the polymer of perdeuterated styrene prepared in toluene by $TiCl_4$.
X and Y: Signals due to the remaining protons in the styrene-d_8 and nitrobenzene-d_5, respectively

same values were obtained from the methyl proton signal at 2.15ppm.

If the chain transfer to solvent(equation 1) is followed by the path (2) or path (3), the regenerated active chain should contain the CHD_2- group at the chain end. The peak at 0.97ppm in the spectrum(Figure 1) should be due to the proton of this partially deuterated methyl group. As mentioned above the spin-lattice relaxation time for this peak was much longer than those for other two peaks. The longer relaxation time should be due to the loss of dipolar relaxation from the two replaced protons. On the other hand, some cocatalyst is usually necessary for the cationic polymerization of styrene by metal halide (PLESCH 1963). In the present work the cocatalyst should be a small amount of water which was admitted incidentally into the reaction mixture.



$$H_2O + TiCl_4 \longrightarrow H^+[TiCl_4(OH)]^- \xrightarrow{\text{styrene-}d_8} CHD_2\text{-}\overset{+}{C}H[TiCl_4(OH)]^-$$

Then the partially deuterated methyl group was introduced into the polymer chain by the initiation reaction as well as the chain transfer reaction. The difference between the amounts of the terminal CHD_2- group and of the toluene fragments may correspond to the amount of the water which existed in the reaction mixture and functioned as a cocatalyst at the begining of the polymerization. It was about 0.1mg from the data in Table 2.

As is shown in Table 2, in the polymerization by $TiCl_4$ 64% of the polymer molecules produced contained the toluene fragments, which were incorporated by solvent transfer reaction. It was reported that the rate constant for monomer transfer was much larger than that for termination reaction in the polymerization of styrene in benzene by $TiCl_4$ (SAKURADA et al. 1958; HIGASHIMURA and OKAMURA 1956a). If the same is assumed in our polymerization, the residual 36% of the polymer molecules should be formed by the monomer transfer reaction and the reciprocal degree of polymerization should be represented by the following equation,

$$\frac{1}{DP} = \frac{k_M}{k_P}\left(\frac{k_S}{k_M}\frac{[S]}{[M]} + 1\right) \qquad (4)$$

where k_P, k_S and k_M are, respectively, the rate constants for propagation, solvent transfer and monomer transfer reactions and [S] and [M] are the concentrations of the solvent toluene and monomer, respectively. Here, the value of $k_S[S]/k_M[M]$ could be estimated to be 64/36 for the polymerization of perdeuterated styrene in toluene by $TiCl_4$. Then the value of k_M/k_P was calculated to be 0.0228, which was level with the k_M/k_P value, 0.02, obtained kinetically by Sakurada et al.

(1958) for the polymerization in benzene by $TiCl_4$. By the substitution of the initial concentrations of solvent and monomer for the [S] and [M] in the equation of $k_S[S]/k_M[M] = 64/36$, the value of k_S/k_M were roughly estimated to be 0.152. Then the value of k_S/k_P was calculated to be 0.0035 by the following equation (5).

$$\frac{k_S}{k_P} = \frac{k_S}{k_M}\frac{k_M}{k_P} \qquad (5)$$

The k_S/k_P thus obtained is also level with that determined for the $TiCl_4$ polymerization in benzene(0.0051) (SAKURADA et al. 1958).

An extensive study is now under way on the various kinds of polymerization and the results will be published in the future.

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