

SOLUBLE POLYACETYLENE OBTAINED WITH RARE-EARTH CATALYST AND SOME ASPECTS OF POLYMERIZATION MECHANISM

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ABSTRACT

Soluble polyacetylene (PA) with well-defined nature has been synthesized with catalyst system $\text{Nd}(i\text{-OPr})_3/\text{AlR}_3$ ($\text{R} = \text{C}_2\text{H}_5$ -, $i\text{-C}_4\text{H}_9$ -) and characterized by IR, Raman and ESR Spectra etc. Number average molecular weight of the soluble specimen were determined by VPO to be about 500g/mol. or lower. The IR and NMR spectra and end group analysis of the soluble polyacetylene fully demonstrate that polymerization of acetylene with rare-earth catalyst is realized through monomer insertion between the transition metal-carbon bond.

Polyacetylene, PA, has been a recent subject of extensive research activities since the discovery of its doping-induced conductivity in 1977^[1,2]. Most studies have been with the silvery, self-sustaining films prepared by solution polymerization of gaseous acetylene with Ziegler-Natta catalyst, as reported by Shirakawa et al. in 1971^[3]. Little is known concerning the mechanism of polymerization of acetylene with Ziegler-Natta catalysts^[4] as well as with rare-earth catalysts as the result of insolubility of such PA films. In this work, we have synthesized for the first time with Ln-catalyst soluble homopolymers of acetylene, which was characterized by IR, Raman, and ESR. Meanwhile, a mechanism of acetylene polymerization has been proposed on the basis of IR and NMR analysis of the end groups of the polymers.

EXPERIMENTAL

1. Materials

Acetylene was purified as previously described^[5]; toluene was used as the solvent. The preparation of tri(*i*-propyloxy)-neodymium ($\text{Nd}(i\text{-OPr})_3$) followed the method depicted in reference [6]. Triethylaluminum and triisobutylaluminum were used as received.

2. Polymerization procedure

In a typical experiment, $\text{Nd}(i\text{-OPr})_3$, toluene and triethylaluminum in calculated amounts

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were added in that order into a flask under an argon atmosphere with stirring. The mixture was stirred for an hour at room temperature, and purified acetylene gas was introduced into the flask. Polymerization immediately occurred with color change and was continued until terminated by adding alcohol. A red resinous polymer resulted after the removal of the minute insoluble materials and the solvent. All operations were carried out under argon atmosphere.

3. Measurements

The IR and NMR spectra were recorded with a Perkin-Elmer 599-B and a JYHG-255 spectrophotometer, respectively, ESR spectra with JES-FE₃AX and NMR spectra with FX-100 spectrophotometer. X-ray diffraction photographs were taken by a flat camera with nickel-filtered CuK α radiation. Measurement of the number average molecular weight (M_n) of the polymers was carried out in a vapor phase osmometer.

RESULTS AND DISCUSSION

1. Characterization of the soluble polyacetylene

IR spectrum of PA as shown in Figure 1 indicates that soluble PA primarily consists of trans configuration as testified by absorption band at 1015cm^{-1} . The bands at 2960, 2925, 2870 and 1465cm^{-1} , which were about in Shirakawa^[3], undoubtedly resulted from the vibrational absorption of certain alkyl groups at the polymer ends. Raman spectrum of the soluble PA, as shown in Figure 2, is rather similar to that of the trans PA film reported previously^[4]. Bands at 1540 and 1130cm^{-1} are assigned to the vibrational absorption of the carbon-carbon double and single bonds, respectively.

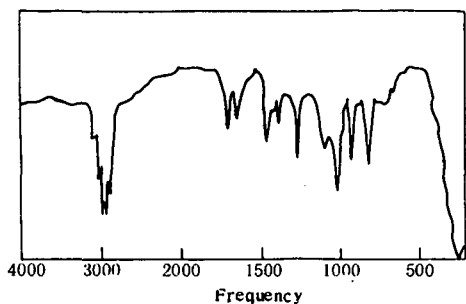


Fig. 1 Infrared spectrum of the soluble PA
Catalyst: Nd (*i*-OC₃H₇)₃/Al(C₂H₅)₃

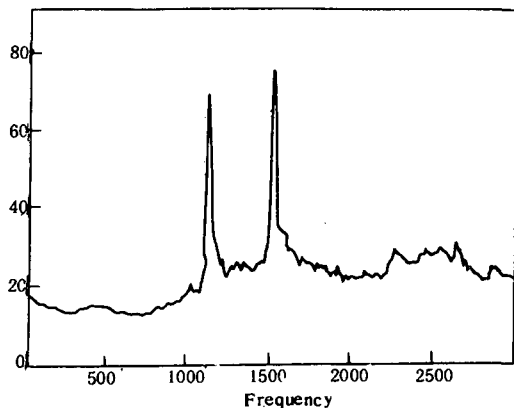


Fig. 2 Raman spectrum of the soluble polyacetylene
Laser = 5145 Å, power 5mW, scanning speed $200\text{cm}^{-1}/\text{min}$

Unlike the insoluble *trans*-PA film, the soluble PA is an amorphous polymer and its X-ray diffraction pattern locates at a Bragg angle of $2\theta = 21^\circ$ as shown in Figure 3. ESR studies indicate that the soluble PA exhibits a singlet absorption with an asymmetric line shape and a line width

(ΔH_{pp}) of 17G. The signal has a g value of 2.0022 which is very close to that of the free electron. As shown in Table 1, the spin density determined at room temperature is 7.1×10^{13} spin/g, much lower than that of the insoluble *trans*-PA film. Data presented in Table 1 clearly demonstrate the great disparity among the different forms of *trans*-PA. This might be attributed to difference in average molecular weight of PA. The number average molecular weight of the soluble PA measured under different conditions is 500g/mol. or so, as seen in Table 2, while that of the insoluble PA films was commonly above 1×10^5 [8,9].

Table 1 Spin densities and ΔH_{pp} values of *trans* PA with various $\bar{M}_n$

<i>trans</i> PA samples	$\bar{M}_n$	Spin densities (e ⁻ /g)	ΔH_{pp} (G)
Soluble PA	$3-5 \times 10^2$	6.6×10^{13}	16-17
PA powder	--	1.5×10^{16}	12-13
Graft PA*	4×10^3	1.6×10^{17}	5
PA film**	2×10^4	2.2×10^{19}	0.3-2.5

* from reference [7], **from reference [14]

Table 2 Number average molecular weight of the soluble PA

Expt. No.	AlR ₃	[Al]/[Nd] (mol. ratio)	Polymn. temp. (°C)	Catalyst concentration 10 ² (M)	$\bar{M}_n$
2	AlEt ₃	10	15	1.5	541
3	"	20	15	1.5	458
1	"	30	15	1.5	356
46	Al(<i>i</i> -Bu) ₂ H	10	15	1.5	340
32	"	20	15	1.5	278
23	AlEt ₃	20	15	0.5	502
21	"	20	15	2.5	321
26	"	20	15	6.5	322
47	"	20	0	6.5	317
26	"	20	20	6.5	322
76	"	20	50	6.5	277

The other component of catalyst is Nd(*i*-OC₃H₇)₃. Testing temperature: 45°C, Solvent: benzene

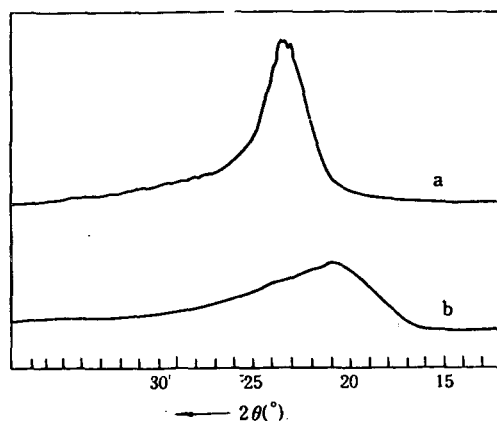


Fig. 3 X-ray diffraction of the *trans* polyacetylene
(a) insoluble PA powder; (b) soluble PA.

2. Mechanism of Polymerization

The concept of monomer insertion in the transition metal-carbon has been widely accepted for Ziegler-Natta Polymerization of diene or vinyl monomers. Insolubility of PA makes it difficult to verify the mechanism in the polymerization of acetylene, because of the non-applicability of the method of end group analysis, a very effective method for polymerization mechanism investigation. Now the soluble PA makes this possible. As discussed before, in the case of monomer insertion, alternation of the groups in the catalyst will be reflected in the structure of the final polymers. Results in Figure 1 and Table 3 fully demonstrate that the soluble PA initiated with the catalyst $\text{Nd}(i\text{-OC}_3\text{H}_7)_3/\text{Al}(\text{C}_2\text{H}_5)_3$ contains an ethyl end group. When $\text{Al}(\text{C}_2\text{H}_5)_3$ in the catalyst is replaced by $\text{Al}(i\text{-C}_4\text{H}_9)_3$, (interesting change comes out on the IR spectrum of polymer obtained, as illustrated in Figure 4) in addition to the vibrational absorption bands of methyl and methylene groups at 2960 , 2870 and 1465cm^{-1} , respectively, split bands at 1385 and 1365cm^{-1} , arising from the vibrational split of the methyl groups in the isopropyl group, are observed which

Table 3 The spectrum bands of the saturated group in the soluble PA

Observed frequency(cm^{-1})	Intensity	Assignment
2960	vs	$\nu_{as}(\text{CH}_3)$
2925	vs	$\nu_{as}(\text{CH}_2)$
2870	vs	$\nu_{as}(\text{CH}_3)$
1465	s	$\delta(\text{CH}_2)$
1375	s	$\nu_s(\text{CH}_3)$

attributed to the characteristic bands of isopropyl group^[10]. Therefore, the polymer end links certainly an isobutyl group. Moreover, the strong absorption band at 910cm^{-1} , characteristic of side ethenyl group in 1,2-polybutadiene^[11,12], demonstrates clearly that an ethenyl group clings to the other end of polymer.

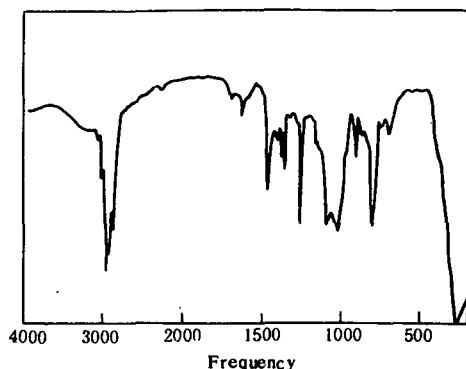
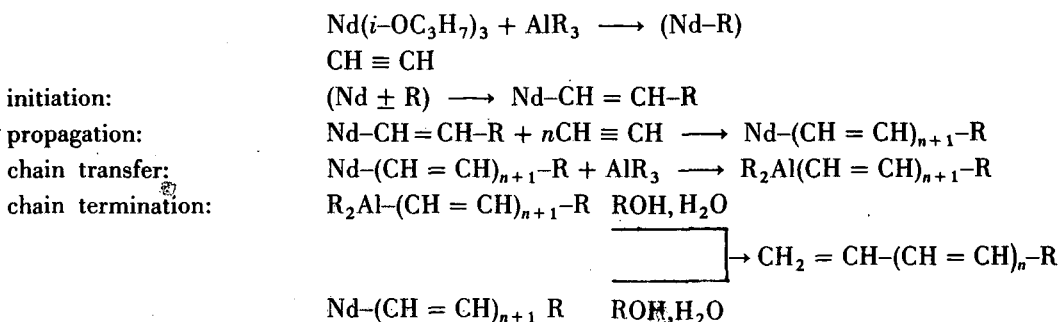


Fig. 4 Infrared spectrum of the soluble polyacetylene.

Catalyst: $\text{Nd}(i\text{-OC}_3\text{H}_7)_3/\text{Al}(i\text{-C}_4\text{H}_9)_3$

Based on the above IR spectrum analysis, a scheme of polymerization of acetylene with $\text{Nd}(i\text{-OC}_3\text{H}_7)_3/\text{AlR}_3$ can be proposed as follows:



Without speculating on the stereochemistry of the catalytically active centers and their transfer reaction with the monomer, the structure of the final polymer derived from this polymerization scheme should be symbolized as $\text{CH}_2 = \text{CH}-(\text{CH}=\text{CH})_n\text{-R}$ ($\text{R} = -\text{CH}_2\text{CH}_3$ or $-\text{CH}_2\text{CH}(\text{CH}_3)_2$).

$^1\text{H-NMR}$ end group analysis has been made to confirm further the scheme proposed. On $^1\text{H-NMR}$ spectra of the soluble specimen, the band at $\delta = 0.826$ ppm is ascribed to the resonance of methyl protons. In conformity with the δ value (4.95 ppm) of the two end protons in side vinyl group of 1,2-polybutadiene^[12,13], the peak at $\delta = 4.97$ ppm is reasonably assigned to the protons in the vinyl groups of the soluble PA's end. Areas under the two defined peaks have been integrated and their ratios are given in Table 4. These values depend on the alkyl-aluminum used. The area ratios, approximaing 1.5, are of the soluble PA obtained with triethylaluminum as a component of catalyst. Similar results are obtained when triisobutylaluminum is used.

Table 4 Resonance peak areas on ^1H -NMR spectra of the soluble PA

Sample No.	AlR_3	Peak area $S_1(\text{cm}^{-1})$	Peak area $S_2(\text{cm}^{-1})$	S_1/S_2
		$\delta = 0.862_{\text{ppm}}$	$\delta = 4.974_{\text{ppm}}$	
8	AlEt_3	8.0	5.5	1.45
67	" "	11.2	7.5	1.49
3	"	7.5	5.0	1.50
69	"	9.5	6.5	1.46
68	"	10.5	7.0	1.50
70	"	9.5	6.5	1.46
22	$\text{Al}(i\text{-Bu})_2\text{H}$	15.0	5.0	3.00
81	"	11.5	4.0	2.88

The other component of catalyst is $\text{Nd}(i\text{-OC}_3\text{H}_7)_3$.

The multi-modal profile of the molecular weight distribution of the soluble PA suggests chain transfer with the monomer be extensive in the polymerization, giving rise to soluble specimens with lower average molecular weight.

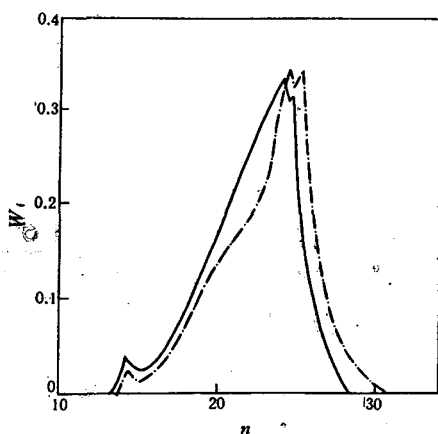


Fig. 5 GPC elution curve of the soluble polyacetylene

Solvent: tetrahydrofuran, room temperature

Keywords:

Soluble polyacetylene; Rare Earth Catalyst

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