

SYNTHESIS OF POLY(VINYLDENE FLUORIDE) WITH LOW CONTENTS OF HEAD-TO-HEAD CHAIN

DUAN Youlu (段友芦), YU Xiuying (俞秀英),

XUE Ying (薛英), ZENG Miaoying (曾淼莹) and JI Shanrong (纪善荣)

(Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai)

ABSTRACT

The relations between polymerization conditions of vinylidene fluoride and contents of head-to-head chain in the polymer have been studied. It shows that the contents of head-to-head chain of the polymer are related to its polymerization temperature, but are not related with the kinds of initiators used. Therefore, poly(vinylidene fluoride) with low contents of head-to-head chain (ca. 3%) can be prepared under lower polymerization temperature. Plot of the contents of A chains against melting points of the polymer is linear, which can be expressed by an equation: $A = 24.8 + 0.362 T_m(^\circ)$.

The studies of piezoelectric property of poly(vinylidene fluoride) have received considerable attention since its piezoelectric activity was found by Kawai in 1969^[1-5]. But as yet, there has not been a completely accepted interpretation of the mechanism responsible for its piezoelectric activity. The piezoelectric activity is generally in relation to the numbers of dipoles in unit volume, and hence in relation to regularity of sequence structure, i.e. the ratios of the contents of head-to-tail chain to head-to-head chain or to tail-to-tail chain in the polymer molecule, as shown in Fig. 1. It illustrates that if there are irregular chains, in which chain B, C and D exist, reverse- CF_2 -dipole must appear in sequence structure of the polymer, its piezoelectric activity will be influenced.

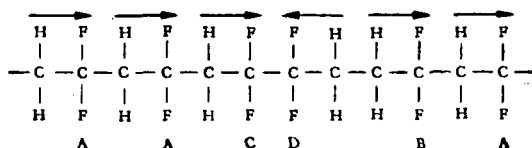


Fig. 1 Sequence structure of poly(vinylidene fluoride)

Therefore, it is very interesting how to synthesize poly(vinylidene fluoride) with low contents of head-to-head chain. Though there is no evidence, the contents of head-to-head chain are generally considered to be in relation to its polymerization temperature^[6]. On the other hand, Liepins et al.^[7] made an attempt to synthesize poly(vinylidene fluoride) with low contents of head-to-head chain using modified Ziegler-Natta catalyst, and poly(vinylidene fluoride) with 3% contents of head-to-head chain was obtained.

In the present work the relations between the contents of head-to-head chain and polymerization temperature or the kinds of initiators in poly(vinylidene fluoride) have been studied.

Poly(vinylidene fluoride) with ca. 3% contents of head-to-head chain has been synthesized by using organic initiator.

EXPERIMENTAL

A 2L autoclave of stainless steel has been used for the polymerization. The autoclave was vacuumed first, swept with gas of vinylidene fluoride twice, and then put into a water bath or oil bath when the required temperature is above 100°C. 1000 ml deionized water and given amount of initiator were added under vacuum and vinylidene fluoride was compressed into the autoclave. Whenever the pressure in the autoclave reduced, a certain amounts of vinylidene fluoride should be added, in order to keep the pressure constant in it during the whole polymerization period. The polymers obtained were pounded to small pieces, then extracted and washed by ethyl alcohol, dried in a vacuum oven at 100°C until constant weight, and their characteristics were determined.

Initiators Diisopropyl peroxydicarbonate (IPP) supplied by Shanghai Liaoyuan Chemical Factory, was kept in an dryice-alcohol mixture after dissolved in acetone with the concentration of 568 mg/ml. Dicyclohexyl peroxydicarbonate (DCPD) supplied by Jiangyin Agricultural Chemical Plant was recrystallized. The contents of DCPD is more than 95%. Di-*t*-butyl peroxide (DTBP) and potassium persulfate were chemical reagent grade. Vinylidene fluoride was supplied by Shanghai Institute of Organic Fluorine Material.

F^{19} NMR spectra of poly(vinylidene fluoride) were measured with NMR spectrometer at 56.4 MHz, 94 MHz and 188 MHz, respectively. The melting temperature of the polymer was determined by means of DSC model CDR-1 in nitrogen atmosphere with heating rate 10°C/min. The top of the peak was taken as its melting point.

RESULTS AND DISCUSSION

1. Determination of the content of head-to-head chain in the polymer by F^{19} NMR

By Wilson's method^[8], the contents of head-to-head chain in poly(vinylidene fluoride) have been measured with F^{19} NMR, as shown in Fig. 2.

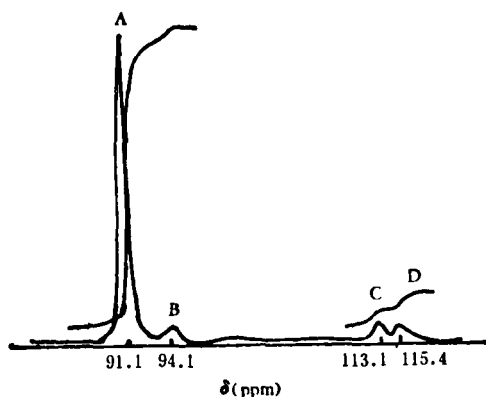


Fig. 2 F^{19} NMR spectra of poly(vinylidene fluoride) (10% DMA, 94 MHz)

A, B, C and D in Fig. 2 are corresponding with Fig. 1, their chemical shifts are 91.1, 94.1, 113.1 and 115.4, respectively (ppm, trifluoroacetic acid as outer reference standard). F^{19} NMR spectra of the polymer measured at 188 and 56.4 MHz are similar to Fig. 2, the only difference is in the concentrations in DMA solutions used. The concentrations of the polymer sample in the solutions used at 188 and 56.4 MHz are ca. 2% and ca. 25%, respectively.

The same samples of poly(vinylidene fluoride) were measured by using different NMR spectrometers, and the integral areas of A, B, C and D were calculated, and then the contents of head-to-tail chain and head-to-head chain were calculated with reference to the method in literature [7], as listed in Table 1.

Table 1 The contents of head-to-tail chain measured by different NMR spectrometers

No. of sample	Integral area								Content ratio of different sequence structure							
	A		B		C		D		A		B		C		D	
	I*	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
24	126.3	70.7	7.8	4.5	8.3	4.8	8.0	4.8	0.8398	0.8337	0.0519	0.0531	0.0552	0.0566	0.0532	0.0566
26	111.2	112.4	6.0	6.4	6.0	5.5	6.5	5.5	0.8574	0.8659	0.0463	0.0493	0.0463	0.0424	0.0501	0.0424
21	159.0	49.9	5.0	2.5	7.0	2.1	7.0	2.1	0.8933	0.8816	0.0281	0.0442	0.0393	0.0371	0.0393	0.0371
29	127.9	103.2	5.4	3.7	5.0	3.7	5.0	3.7	0.8925	0.9029	0.0377	0.0324	0.0349	0.0324	0.0349	0.0324
KF-1000	167.5	84.5	6.8	4.0	5.6	3.2	6.5	3.2	0.8981	0.8904	0.0365	0.0421	0.0300	0.0337	0.0349	0.0337

* I—data measured by 188 MHz F^{19} NMR;

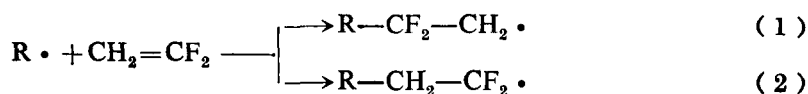
II—data measured by 94 MHz F^{19} NMR.

Table 1 illustrates the ratios of A, B, C and D chain of the same polymer sample measured at 188 MHz and 94 MHz are nearly the same. The relative errors of the contents of A chain are generally within 1%.

The regularity of sequence structure of poly(vinylidene fluoride) in literature can be expressed by several ways, such as using percent of the contents of head-to-head chain (i.e. C chain) or tail-to-tail chain (i.e. B chain) [7], of head-to-tail chain (i.e. $A + \frac{1}{2}B + \frac{1}{2}C = A + B$) [9,10] and of reverse monomer repeat unit [11]. The percent of head-to-tail chain (i.e. $A + \frac{1}{2}B + \frac{1}{2}C = A + B$) of KF-1000 measured is ca. 93%, and it is as near as that in literature [9,10].

2. The kinds of the initiators and the structure regularity of poly(vinylidene fluoride)

According to mechanism of initiation reaction, the initiation of vinylidene fluoride is as follows:



The nature of the free radical $R \cdot$ formed from initiator influences the ratio of rate of these two reactions [12]. The contents of head-to-head chain of poly(vinylidene fluoride) polymerized at same temperature (70°C), using by means potassium persulfate and IPP as

initiators, have been compared. The sequence structure of poly(vinylidene fluoride) polymerized at 25°C with IPP as an initiator was also compared with that of it polymerized with modified Ziegler-Natta catalyst by Liepins et al., as given in Table 2.

Table 2 The content of head-to-tail chain of poly(vinylidene fluoride) polymerized with different initiators

Initiator	Temp. of polymn. (°C)	Content ratio of different sequence structure			
		A	B	C	D
K ₂ S ₂ O ₈	70	86.9	4.3	4.4	4.4
K ₂ S ₂ O ₈	70	87.5	4.1	4.1	4.1
IPP	70	86.7	4.5	4.3	4.5
IPP	70	86.5	4.5	4.6	4.4
IPP	25	90.4	2.8	3.4	3.5
IPP	25	90.1	2.8	3.8	3.3
B(i-Bu) ₃ / O ₂	room temp.	90.6	3.2	3.1	3.1
Et ₃ Al / TiCl ₄ / CH ₂ Cl ₂ *		—	2.7	~3.0	—

* from literature[7].

From Table 2 it shows that the regularities of molecular sequence structure of poly(vinylidene fluoride) polymerized at same temperature but with different initiators are nearly the same. The percent of the contents of A chain of poly(vinylidene fluoride) polymerized at 70°C with potassium persulfate as an initiator is ca. 87%, which is as same as that at 70°C with IPP as an initiator. The content percent of A chain of poly(vinylidene fluoride) polymerized at 25°C with IPP as an initiator is ca. 90%, which is as same as that at room temperature using B(i-Bu)₃ / O₂ as catalyst.

Electric properties of free radical formed from decomposing initiators in Table 2 are quite different. Potassium persulfate and IPP, for examples, decompose as follows:



SO₄^{·-} is a negatively charged free radical. (CH₃)₂CHO· is a little electronegative free radical, because methyl group is an electron donor and it is less negative than the former. Therefore, their selectivities of attacking the two carbon atoms in vinylidene fluoride molecule, i.e. the ratio of reaction (1) to reaction (2), are different. It seems certain that the regularities of molecular structure of the polymer would be different. Only two monomer repeat units in the end of the polymer chains have been influenced by the initiation according to the mechanism of the termination by combination. In view of the molecular weights of poly(vinylidene fluoride) which are generally between ten thousands and a hundred thousands, there are more than one thousand of monomer repeat units in a molecule of the polymer. That is to say, there are only 0.1—0.2% structural regularities of the polymer influenced by the initiation. It is the reason why Liepins et al. using modified Ziegler-Natta catalyst could not obtain

the polymer with even lower content of head-to-head chain.

3. Dependence of sequence structure of the polymer chain upon polymerization temperature

The ratios of head-to-tail chain, to head-to-head chain and to tail-to-tail chain in molecular chains of poly(vinylidene fluoride) obtained under different temperatures were determined by NMR. The results were in Table 3. All the samples in Table 3 were polymerized with IPP as an initiator, except that polymerized at 135°C with DTBP as an initiator.

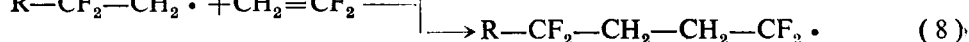
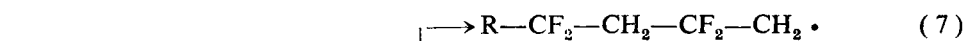
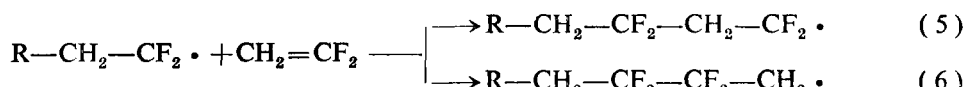
Table 3 Data of NMR of poly(vinylidene fluoride) polymerized under different temperatures*

No.	Polymn. temp. (°C)	T_m (°C)	Integral area of NMR				Content ratio of different sequence structure			
			A	B	C	D	A	B	C	D
37	25	180	130.7	4.0	4.9	5.0	0.9039	0.0277	0.0339	0.0346
39	25	180	91.8	2.8	3.9	3.4	0.9009	0.0275	0.0383	0.0334
56	25	180	161.0	5.0	6.6	6.7	0.8979	0.0279	0.0368	0.0374
40	25	180	166.8	4.5	6.4	6.5	0.9055	0.0244	0.0347	0.0353
42	25	180	153.0	6.0	5.2	6.0	0.8989	0.0353	0.0306	0.0353
8	55	176	158.0	6.5	7.5	7.5	0.8827	0.0363	0.0419	0.0419
16	55	177	114.0	4.9	4.9	4.9	0.8859	0.0381	0.0381	0.0381
18	55	177—178	117.6	5.4	5.4	5.4	0.8789	0.0404	0.0404	0.0404
55	55	176	141.0	7.7	7.0	7.0	0.8704	0.0432	0.0432	0.0432
2	70	172—173	99.0	4.9	5.0	5.0	0.8690	0.0430	0.0439	0.0439
3	70	172—173	126.9	5.9	5.9	5.9	0.8677	0.0438	0.0438	0.0438
4	70	173	129.3	6.8	7.5	7.3	0.8669	0.0451	0.0437	0.0444
24	135	165	126.3	7.8	8.3	8.0	0.8398	0.0519	0.0552	0.0532

* calculated with reference to the method in literature [7].

It shows in Table 3 that the regularities of sequence structure of the polymer increased with decreasing polymerization temperature. This is in agreement with the result given in literature [9]. The regularities of sequence structure of the polymer polymerized at 25°C and 135°C were 92—93% and 89—90% respectively and they are very much close to the values given in literature [9], when they were represented by the content of head-to-tail chain, i.e. $A + \frac{1}{2}B + \frac{1}{2}C$.

The chains in reverse manner could take place in the propagation step according to the mechanism of polymerization, that is,



As for the activation energy for a reaction, the activation energy for reactions (6) and (8) is higher than that for reactions (5) and (7). The possibilities of both reactions (6) and (8) became greater with increasing polymerization temperature so that more chains in reverse manner would take place.

4. The relation between melting temperature and chain regularity of the polymer

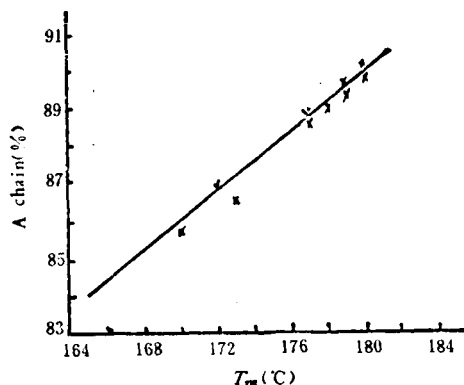


Fig. 3 The relation between chain regularity and melting point of the polymer

Fig. 3 is the plotting of contents of A chains against melting point of the polymer listed in Table 4. The relation between the contents of A chains and melting points could be expressed by an equation:

$$A = 24.8 + 0.362 \times T_m (\%). \quad (9)$$

Table 4 Melting temperature and chain regularities of poly(vinylidene fluoride)

No.	24	15	2	55	8	16	50	51	31	21	42	56	59	KF-1000
T_m (°C)	165	170	172	173	176	177	177	178	179	179	180	180	180	180
Content of A chain	84.0	85.7	86.9	86.6	88.3	88.6	88.6	89.0	89.6	89.3	89.9	89.8	90.1	89.8

The contents of A chain of the polymer could be calculated on its melting point according to this equation. The comparison of the experimental data with calculated data could be seen in Table 5, their errors were within 1%.

The calculated content of A chain of KF-1000 in Table 5 was 89.6%. In consideration of the contents of B, C and D chain were nearly the same, the content of head-to-tail chain, i.e. A + B, should be $89.6 + \frac{1}{2}(100 - 89.6) = 93.1(\%)$, which was very much close to the value given in literature [9,10]. The melting point of poly(vinylidene fluoride) produced by Pennwalt Corp. is 160°C according to the literature [6]. By equation (9) the calculated value A was 82.7%. So the content of head-to-head chain is $\frac{1}{2}(100 - 82.7) = 5.8(\%)$, which is close to the experimental data (6.8%) in the literature.

Table 5 The comparison of the experimental content of A chain of the polymer with calculated one

No.	T_m (°C)	Content of A chain (%)		Error
		experimental	calculated	
42	180	89.9	90.0	+0.1
50	177	88.6	88.9	+0.3
26	173	86.6	87.4	+0.8
55	171	87.0	86.7	-0.3
24	165	84.0	84.5	+0.5
KF-1000	179	89.8	89.6	-0.2

REFERENCES

- [1] Kawai, H., *Jpn. J. Appl. Phys.*, **1969**, 8, 975.
- [2] Kepler, R. G., Anderson, R. A., *J. Appl. Phys.*, **1978**, 49, 4490.
- [3] Lovinger, A. J., Wang, T. T., *Polymer*, **1979**, 20, 725.
- [4] Banzi, S. S., Kao, K. J., Perlman, M. M., *J. Polym. Sci., Polym. Phys. Ed.*, **1980**, 18, 1945.
- [5] Toshiharu Yagi, Masayoshi Tatemoto, Jun-ichi Sako, *Polymer J.*, **1980**, 12, 209.
- [6] Doll W. W., Lands, J. B., *J. Appl. Polym. Sci.*, **1970**, 14, 1769.
- [7] Liepins, R., Surles, J. R., Morosoff, N., Stannett, V. T., Timmons, M. L., Wortman, J. J., *J. Polym. Sci., Polym. Chem. Ed.*, **1978**, 16, 3039.
- [8] Wilson, C. W., *J. Polym. Sci. Part A*, **1963**, 1, 1305.
- [9] 里川孝臣, ふつ素樹脂, 日刊工業新聞社, **1969**.
- [10] Osaki, S., Ishida, Y., *J. Polym. Sci., Polym. Phys. Ed.*, **1975**, 13, 1071.
- [11] Welch, G. J., *J. Polym. Sci., Polym. Phys. Ed.*, **1976**, 14, 1683.
- [12] Jenkins, A. D., Ledwith, A., *Reactivity, Mechanism and Structure in Polymer Chemistry*, A Wiley-Interscience Publication, New York, **1974**, p. 49.