Studies on Microstructure of Poly(trifluoroethylene) Chain by Fluorine-19 NMR and Monte Carlo Simulation

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ABSTRACT: An investigation was carried out on the molecular microstructure of poly(trifluoroethylene) (PTRFE). With the high-resolution ^{19}F -NMR spectrum of PTRFE and the computer simulation of the same polymerization system, the amount of backward-added monomer units and their distribution in polymer chain were estimated. The distribution is represented by the reactivity ratios of head- and tail-position of the unsymmetrical monomer to each propagating polymer radical. The assignment of absorption peaks of ^{19}F -NMR spectrum of PTRFE was made on an empirical basis, and four possible structures, containing 5 carbon atoms along the polymer chain with a $-\text{CF}_2-$ group as the central group, were figured out. The percentage of backward-added trifluoroethylene (TRFE) in the PTRFE chain polymerized at 22°C was 50%. Denoting CFH-position and CF_2 -position in TRFE ($\text{CFH}=\text{CF}_2$) by B and A, respectively, the reactivity ratio of B and A of TRFE to the $---\text{CF}_2\cdot$ radical was estimated as $B/A=1/0.75$ and that of TRFE to the $---\text{CFH}\cdot$ radical was $1/1.33$.

KEY WORDS Microstructure / Poly(trifluoroethylene) / Fluorine-19 NMR / Trifluoroethylene / Monte Carlo Simulation / Head-to-Tail Structure / Head-to-Head Structure /

Since the high-resolution fluorine-19 NMR study was made by Ferguson on vinylidene fluoride (VDF)-hexafluoropropylene copolymers and by Naylor and Lasoski on poly(vinylidene fluoride) (PVDF), there have been published in literature a number of ^{19}F NMR studies¹⁻¹⁵ on the molecular microstructures of fluorinated polymers. The ^{19}F NMR is effective for studying the molecular microstructure of fluorinated polymers, since the fluorine chemical shifts are so large compared with those of a proton. In the series of fluorinated ethylene polymers from poly(vinyl fluoride) (PVF) to PTRFE, the molecular microstructure of PVF^{4,10} and PVDF^{1,3,4,10} have been studied in detail by many authors, while that of PTRFE,^{2,7} by only a few. The first work on PTRFE was that of Naylor and Lasoski.¹ They studied the chemical shifts in the structure $-\text{CF}_2-\text{CFH}-\text{CF}_2-$ and $-\text{CFH}-\text{CF}_2-\text{CFH}-$, but gave no comments on the molecular microstructure. The work of Wilson⁷ indicated the presence of both head-to-tail and head-to-head linkages and tacticity defects in the PTRFE chain.

On the other hand, Tedder and his coworkers^{16,17} studied the reactivity ratios of head- and tail-position of vinyl fluoride (VF), VDF and TRFE to methyl radical ($\text{CH}_3\cdot$) and fluorinated methyl radicals ($\text{CFH}_2\cdot$, $\text{CF}_2\text{H}\cdot$ and $\text{CF}_3\cdot$), in the gaseous state at a high temperature. They reported that the regularity of reaction position decreased in the order, VDF, VF and TRFE.

The purpose of this study is, first, to assign the ^{19}F -NMR peaks of PTRFE and, second, to estimate the amount of backward-added monomer units and their distribution in the polymer chain by applying Monte Carlo simulation to NMR data. This distribution is represented by the reactivity ratios of the head- and tail-positions in the monomer. Only the assignment of NMR peaks and comparison of their intensity ratios are not sufficient to estimate the molecular microstructure. For instance, the sequence of the tail-to-head addition are also detected as a head-to-tail addition in the NMR spectrum. The NMR spectrum reflects only a limited local structure.

EXPERIMENTAL

Material

PTRFE was prepared by bulk polymerization at 22°C using 3,5,6-trichloroperfluorohexanoyl peroxide as an initiator.

Instrument

High-resolution ^{19}F -NMR spectrum was measured with a Hitachi-Perkin-Elmer R-20B spectrometer at 35°C in acetone, using α,α,α -trifluorotoluene (BTF) as a reference.

RESULTS AND DISCUSSION

NMR Assignment

Figure 1 shows the 56.45-MHz ^{19}F -NMR spectrum of PTRFE in the $-\text{CF}_2-$ region. The main resonance peaks are designated as H, I, and J (in the order of increasing magnetic field). The magnetic field scale is given in parts per million (ppm) upfield from a BTF resonance. The chemical shifts are expressed by adding 63.7 ppm to each original value. If the addition of the monomer $\text{CFH}=\text{CF}_2$ to a growing chain end occurs in either a forward or backward manner to form a new end $-\text{CFH}-\text{CF}_2\cdot$ or $-\text{CF}_2-\text{CFH}\cdot$, respectively, the following four types of microstructures will be generated as part of a chain consisting of one central $-\text{CF}_2-$ group and its two front and rear groups.

- st. (1) $-\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-$
- st. (2) $-\text{CFH}-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-$
- st. (3) $-\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CF}_2-\text{CFH}-$
- st. (4) $-\text{CFH}-\text{CFH}-\text{CF}_2-\text{CF}_2-\text{CFH}-$

If there is no backward addition, the resulting chain should contain only st. (1). The st. (2), (3), and (4) originate from backward-added monomer units, apart from their content and distribution. As a typical example, let us consider three polymer segments.

Segment (a) $-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-$
 $\text{CF}_2-\text{CFH}-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-$

Segment (b) $-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CF}_2-\text{CFH}-$
 $\text{CF}_2-\text{CFH}-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-$

Segment (c) $-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CF}_2-\text{CFH}-$
 $\text{CFH}-\text{CF}_2-\text{CF}_2-\text{CFH}-\text{CFH}-\text{CF}_2-$

Segment (a) has one backward-added monomer unit as underlined, and segment (b) and (c) have two, but with different distributions. It is obvious that an atomic sequence including a central $-\text{CF}_2-$ group has one of the four microstructures st. (1), (2), (3), and (4) mentioned above. As shown in Figure 1, there are three peaks H, I, and J in ^{19}F -NMR spectrum of PTRFE, while the number of microstructures which may correspond to these is four. This suggests that one of the three peaks should correspond to two structures. Taking into account the empirical rule of ^{19}F -NMR concerning the relation between chemical shifts and the molecular microstructure,⁴ we may expect that four NMR peaks in $-\text{CF}_2-$ region will align in the order of st. (1), (2), (3), and (4), from low to high magnetic field. Therefore, peak H must be derived from st. (1) alone or from st. (1) and (2), and peak J from st. (4) alone or from st. (3) and (4), respectively. However, it is hard to from conceive that these peaks are derived from two structural components. The st. (2), though resembling st. (1) up to the first neighbors of the central $-\text{CF}_2-$, can not be expected to give the same effect on the ^{19}F -NMR chemical shift.⁴ Thus, peak H is tentatively assigned to st. (1). In the same way, peak J is assigned to st. (4). Accordingly, it is expected that peak I is derived from both st. (2) and (3). Table I shows the effect on the ^{19}F -NMR chemical shift of $-\text{CH}_2-\text{CF}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CF}_2-\text{CF}_2-$, $-\text{CFH}-\text{CF}_2-\text{CFH}-$, and $-\text{CFH}-\text{CF}_2-\text{CF}_2-$ in the CF_2- region.^{1,2} Considering the difference in the measured magnetic field strength (30 MHz and 40 MHz), it may be expected that the effect on the chemical shift of $-\text{CFH}-\text{CF}_2-\text{CFH}-$ relative to $-\text{CH}_2-\text{CF}_2-\text{CF}_2-$ is similar, in magnitude, to that

Figure 1. ^{19}F -NMR spectrum of PTRFE in $-\text{CF}_2-$ region at 56.45 MHz and 35°C in acetone. BTF is the reference and the chemical shifts are expressed by adding 63.7 ppm to each original value.

of $-\text{CFH}-\text{CF}_2-\text{CF}_2-$. Accordingly, it is expected that two st. (2) and (3) have the same effect on the ^{19}F -NMR chemical shift as the central $-\text{CF}_2-$ group, since they have a common second neighbor structure. Thus, it was decided that both peaks of st. (2) and (3) overlap in the NMR spectrum and are observed as peak I. These results are summarized in Table II.

Table I. Chemical shift of a carbon triad structure in the $-\text{CF}_2-$ region

Structure	Chemical shift, ^a ppm	Magnetic field strength, MHz
$-\text{CH}_2-\text{CF}_2-\text{CH}_2-$	13.3 ^b	30
$-\text{CH}_2-\text{CF}_2-\text{CF}_2-$	36.6 ^b	30
$-\text{CFH}-\text{CF}_2-\text{CFH}-$	38.3 ^b	30
$-\text{CH}_2-\text{CF}_2-\text{CH}_2-$	14.3 ^c	40
$-\text{CH}_2-\text{CF}_2-\text{CF}_2-$	38.4 ^c	40
$-\text{CFH}-\text{CF}_2-\text{CF}_2-$	41.3 ^c	40

^a The magnetic field scale is given in parts per million (ppm) upfield from a trifluoroacetone reference.

^b Data taken from ref 1.

^c Data taken from ref 2.

Table II. ^{19}F -NMR chemical shifts in poly(trifluoroethylene) (PTRFE)

Peak	Chemical shifts, ^a ppm	Structure	Intensity ^b ratio
H	119.6	$-\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-$	0.30
I	122.7	$-\text{CFH}-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CF}_2-$ $-\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CF}_2-\text{CFH}-$	0.50 ^c
J	125.9	$-\text{CFH}-\text{CFH}-\text{CF}_2-\text{CF}_2-\text{CFH}-$	0.20

^a The magnetic field scale is given in parts per million upfield from a BTF resonance. The chemical shifts are expressed by adding 63.7 ppm to each original value.

^b Calculated from peak areas and normalized to unity.

^c Peak I is composed of two components, and is expressed by the sum of these two components.

Change of Molecular Microstructure

Let us denote an unsymmetrical monomer as $\text{B}=\text{A}$, where A represents the head-position and B, the tail-position. In the case of TRFE, the symbol A is CF_2 and B is CFH. There are two propagating radicals, $---\text{A}\cdot$ and $---\text{B}\cdot$, and two reaction positions, A and B, in the monomer. In this report, we adopt the copolymerization theory of the con-

ventional terminal model.¹⁸ Denote the kinetic constant by K_{bb} , for the propagating reaction,

Similarly, three other kinetic constants K_{ba} , K_{ab} , and K_{aa} are defined for these reactions,

Now, we put $K_{aa}/K_{ab}=x$ and $K_{bb}/K_{ba}=y$, then the parameters x and y represent the relative reactivity ratios of head- and tail-position of unsymmetrical monomer. We represent by $P(\text{BB})$ the probability that a propagating radical $---\text{B}\cdot$ is attached to an A-position and a radical $---\text{B}\cdot$ is again generated. In a similar way, $P(\text{BA})$, $P(\text{AB})$, and $P(\text{AA})$ are defined. Thus, $P(\text{BB})$, $P(\text{BA})$, $P(\text{AB})$, and $P(\text{AA})$ are given by

$$P(\text{BB}) = \frac{K_{bb}(---\text{B}\cdot)(\text{M})}{K_{bb}(---\text{B}\cdot)(\text{M}) + K_{ba}(---\text{B}\cdot)(\text{M})} = \frac{y}{y+1} \quad (1)$$

$$P(\text{BA}) = 1 - P(\text{BB}) = \frac{1}{y+1} \quad (2)$$

$$P(\text{AB}) = \frac{K_{ab}(---\text{A}\cdot)(\text{M})}{K_{aa}(---\text{A}\cdot)(\text{M}) + K_{ab}(---\text{A}\cdot)(\text{M})} = \frac{1}{x+1} \quad (3)$$

$$P(\text{AA}) = 1 - P(\text{AB}) = \frac{x}{x+1} \quad (4)$$

where (M) is the concentration of the monomer, and $(---\text{B}\cdot)$ and $(---\text{A}\cdot)$, that of the propagating radicals. If the parameters x and y are determined, we can calculate the relative intensity of each peak in the NMR. We simulated many polymers, actually 289 polymers, changing both parameters x and y , in eq 1, 2, 3, and 4, and calculated the intensity of the four possible sequences of 5 letters having A at the middle, as well as the amount of backward-added monomer units $-\text{A}-\text{B}-$.

Figure 2 shows the change in the percentage of forward-added monomer units when numerical values of the two parameters x and y are varied from 0.01 to 100. The degree of polymerization of each polymer was about 10000. This range of parameters x and y will cover most cases of practical interest. The percentage of forward-added monomer units becomes large when the parameter x takes on a high value and parameter y , a small value, respectively. On the contrary, this percentage becomes small when

Figure 2. Change in the percentage of forward-added monomer units when the parameters x and y change from 0.01 to 100, respectively. The numerical values of the percentage of forward-added monomer units are indicated on the diagram.

x takes on a small value and y , a high value, respectively. Many polymers, having the same amount of forward-added monomer units but different distributions, are derived from combinations of parameters x and y . If both x and y are greater than unity, the microstructure becomes blocky, while if x and y are close to unity, it becomes random. When x and y are less than unity, the microstructure becomes alternate.

For example, when both x and y are 100, the percentage of forward-added monomer units is 50% as shown in Figure 2, and they are distributed

blockishly. When x and y are unity, the percentage of forward-added monomer units is 50%, but they are distributed randomly; when x and y are 0.01, the percentage of forward-added monomer units is again 50% and these units are distributed alternately. These changes in microstructures are reflected by the intensity of the NMR peaks. Figure 3 shows the change in the fraction of four local microstructures $-A-B-A-B-A-$, $-B-B-A-B-A-$, $-A-B-A-A-B-$ and $-B-B-A-A-B-$ when the parameter $x (=y)$ changes from 0.01 to 100, for which the percentage of forward-added monomer units is assumed to be 50%.

Reactivity Ratio of Head- and Tail-Positions

We have estimated the microstructure of PTRFE from the standpoint of backward-added monomer units and their distribution in the polymer chain by comparing the polymerized PTRFE with the computer simulated polymers, with respect to the intensity of each peak appearing in the NMR spectrum, *i.e.*, the fraction of each structure which containing 5 carbon atoms along the polymer chain with a $-CF_2-$ group as the central group. The intensity ratio of polymerized PTRFE is listed in Table II. We select from the simulated 289 polymers one polymer which show the best fit to this PTRFE. In this way, we found that the percentage of backward-added monomer units in PTRFE chain polymerized at 22°C was 50%, and the parameters x and y were 1.33 and 1.33, respectively. Accordingly, denoting the CFH-position and CF_2 -position in TRFE ($CFH=CF_2$) as B and A, respectively, we estimated the reactivity ratio of B and A to the ---

Figure 3. Changes in the fractions of four local microstructures when the parameter $x (=y)$ changes from 0.01 to 100; *i.e.*, the percentage of the forward-added monomer units is assumed to be 50%. The curves $-B-B-A-B-A-$ and $-A-B-A-A-B-$ overlap.

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101000001000000110010110100111100000000111110101101101010000010000010
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01010111101000011111110100011011111100100000011011100000001010000
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Figure 4. Schematic diagram of PTRFE molecules. The symbols 0 and 1 represent forward-added and backward-added monomer units, respectively.

$\text{CF}_2\cdot$ radical as $B/A=1/0.75$ and that to the $---\text{CFH}\cdot$ radical as $1/1.33$. The TRFE monomer is thought to be polymerized in a random state; *i.e.*, there is no difference between head- and tail-positions in the adding reactions.

This irregularity of TRFE agreed well with the results of Tedder and coworkers^{16,17} and the study for TRFE-isobutylene copolymer.¹⁵

Table III shows the reactivity ratio of head- and tail-positions of TRFE to two propagating radicals ($---\text{CFH}-\text{CF}_2\cdot$ and $---\text{CF}_2\text{CFH}\cdot$), methyl radical ($\text{CH}_3\cdot$), and fluorinated methyl radicals ($\text{CFH}_2\cdot$, $\text{CF}_2\text{H}\cdot$, and $\text{CF}_3\cdot$), at various temperatures. From the similarity in molecular structures, we may con-

clude that the reactivity of the propagating radical $---\text{CH}_2\cdot$ is similar to that of the intermediate radical of $\text{CH}_3\cdot$ and $\text{CFH}_2\cdot$, and furthermore, that the reactivity of $---\text{CFH}\cdot$ is similar to that of $\text{CFH}_2\cdot$ and $\text{CF}_2\text{H}\cdot$. Finally, the reactivity of $---\text{CF}_2\cdot$ is similar to that of $\text{CF}_2\text{H}\cdot$ and $\text{CF}_3\cdot$. Thus, there is a good agreement in the reactivity ratios of the reacting positions of TRFE to each corresponding radical, although there are many differences in reaction system, as shown in Table III.

In Figure 4, the generated polymer chains of PTRFE formed under the above condition are shown. The symbols 0 and 1 represent the forward-added and backward-added monomer units, respectively.

This method may be applied to other polymers consisting of unsymmetrical olefins.

Table III. Reactivity ratio of tail- and head-positions (B/A) of trifluoroethylene (TRFE)

Radical	Reaction temp, °C	B/A
$---\text{CF}_2-\text{CFH}\cdot$	22	1/1.33
$---\text{CFH}-\text{CF}_2\cdot$	22	1/0.75
$\text{CH}_3\cdot$	150	1/7.26 ^a
$\text{CFH}_2\cdot$	164	1/2.04 ^b
$\text{CF}_2\text{H}\cdot$	164	1/1.07 ^b
$\text{CF}_3\cdot$	164	1/0.50 ^b

^a Data taken from ref 16.

^b Data taken from ref 17.

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