



# Influence of alternating sequential fraction on the melting and glass transition temperatures of ethylene–tetrafluoroethylene copolymer

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## ABSTRACT

The melting ( $T_m$ ) and glass transition ( $T_g$ ) temperatures of a series of ethylene (E)–tetrafluoroethylene (TFE) copolymer (ETFE) have been found to show unique dependence on the TFE content with the minimal and maximal points. These behaviors have been interpreted successfully on the basis of the degree of alternation of E and TFE monomeric units along the skeletal chain. The melting point of a perfectly alternating copolymer is estimated to be 295 °C on the basis of the dependence of  $T_m$  using a modified Flory's equation. The corresponding  $T_g$  was estimated as 145 °C by applying a modified Gibbs–Dannation's equation.

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## 1. Introduction

Ethylene (E)–tetrafluoroethylene (TFE) copolymer (ETFE) is a melt-processable fluoropolymer having excellent weatherability, thermal and chemical stability [1]. ETFE is used as an insulator for wires and cables, a coating for anticorrosion, and films for green house. ETFE is known to show high probability of alternating array of E and TFE monomeric units along the chain. The degree of alternation of E and TFE monomer units is dependent on the E/TFE content and the maximal alternating sequential fraction is 0.92 for the copolymer with 50 mol% TFE content [2,3]. The ETFE copolymer showing the ideal alternation of 1.0 has not yet been synthesized.

The crystal structure and physical properties of an alternating copolymer are different from those of the corresponding random copolymers [2–20]. It is important to clarify the TFE content dependence of the physical properties for a series of ETFE copolymers, especially the melting ( $T_m$ ) and glass transition temperatures ( $T_g$ ) as the basic thermal properties. The composition dependence of  $T_m$  and  $T_g$  was reported at first for the samples with limited TFE content [3,5,8] and then for a series of copolymer with a wide range of TFE content [15,18]. The  $T_m$  and  $T_g$  change continuously between the lowest values 137 °C and –128 °C of polyethylene and the highest values 327 °C and 131 °C of polytetrafluoroethylene (PTFE), respectively. One unique point can be noticed for the thermal behavior of ETFE copolymers. As will be shown later, the  $T_m$  and  $T_g$  show the maximal values at 50 mol% TFE content and the minimal

point at around 70 mol% TFE content. These behaviors are observed only for ETFE copolymers and cannot be found at all for any other kinds of copolymers as long as our literature search was made thoroughly. For example the  $T_m$  and  $T_g$  of isobutylene-TFE alternating copolymer (IBTFE) were reported to show the maximal value at 50 mol% TFE content but no minimal point [21]. The  $T_m$  of the perfectly alternating IBTFE copolymer was predicted to be 218 °C on the basis of Flory's equation.

In the present paper, we will reveal the reasons for the complicated behavior of  $T_m$  and  $T_g$  of ETFE copolymers and to estimate the  $T_m$  and  $T_g$  of the perfectly alternating ETFE copolymer for the first time.

## 2. Experimental

ETFE copolymers were synthesized by radical polymerization in fluoro-solvent [22,23]. The monomer composition was controlled to be almost constant by recharging the consumed monomer by monitoring the composition of the produced polymer during the reaction [23]. The copolymer composition was determined by elementary analysis for fluorine content as listed in Table 1. The ETFE copolymer with 50 mol% TFE content, for example, is named here the TFE 50 copolymer.

Unoriented films of 200 μm thickness were prepared by compression mold at 300 °C followed by quenching in a water-cooled press instrument. The  $T_m$ 's were measured by a DSC Q100 (TA instrument inc.). The sample was once heated up to 320 °C and cooled to 25 °C, and then the  $T_m$  was measured as an endothermic

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**Table 1**  
Composition of ETFE copolymers determined by elementary analysis.

	Polymer composition / mol%	
	TFE	E
TFE 39	38.9	61.1
TFE 50	50.0	50.0
TFE 54	53.5	46.5
TFE 60	60.2	39.8
TFE 65	64.9	35.1
TFE 71	71.4	28.6

peak in the 2nd heating process. The heating and cooling rates were 10 °C/min.

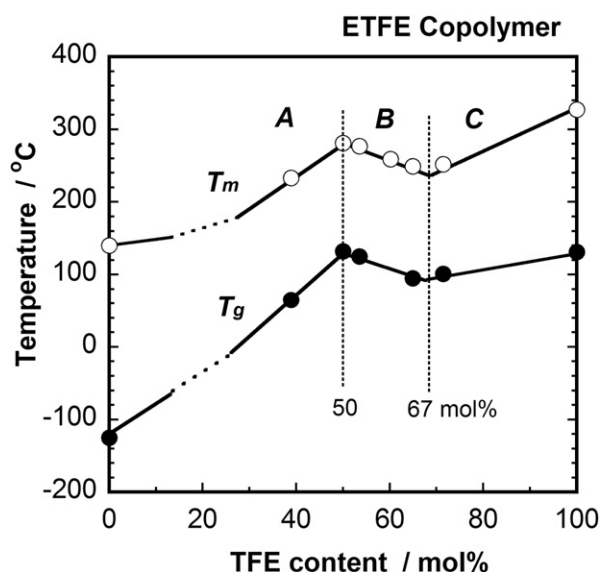
### 3. Results and discussion

Fig. 1 shows the TFE content dependence of  $T_m$  and  $T_g$ , where the  $T_g$  was already reported in our previous paper [17]. Both of  $T_g$  and  $T_m$  show the maximal points at about 50 mol% and the minimal points at around 70 mol%. It might be possible to classify the thermal behavior of ETFE copolymers into 3 groups, A, B and C as shown in Fig. 1.

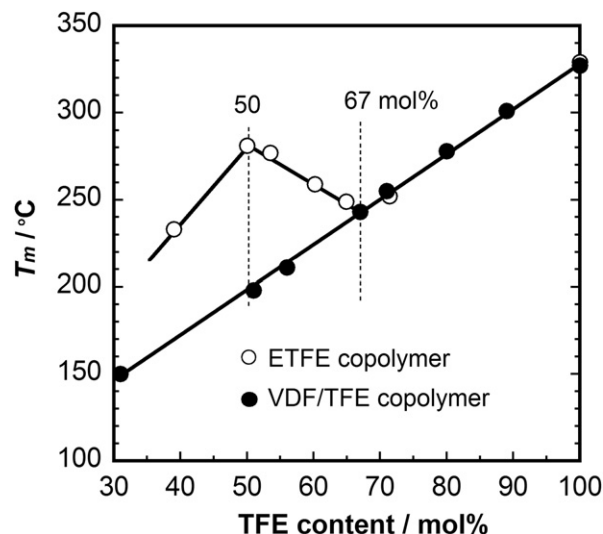
#### 3.1. Melting temperature

The behavior of ETFE copolymers is different from those of general random copolymers. For example, Fig. 2 shows the TFE content dependence of  $T_m$  measured for a series of random copolymer of vinylidene fluoride and TFE (VDF/TFE) in comparison with the ETFE case [24,25]. The monomer reactivity ratios of VDF/TFE random copolymer  $r_1$  and  $r_2$  are 0.38 and 0.36, respectively, where  $r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$  and  $k_{ij}$  is the rate constant of the copolymerization reaction between the two monomers, TFE is monomer 1 and VDF is monomer 2 [25].

The  $T_m$  of VDF/TFE copolymer increases almost linearly with an increase of TFE content in the range of 30–100 mol%. As pointed above, the  $T_m$  of ETFE copolymer has the maximal and minimal values. The maximal  $T_m$  is observed for the TFE 50 mol% copolymer, which may come from the highest alternating sequential fraction of 92% estimated for this copolymer [2,3]. It is expected reasonably that an ideal ETFE copolymer with perfect alternation of two kinds



**Fig. 1.** TFE content dependence of  $T_m$  and  $T_g$  observed for a series of ETFE copolymers.



**Fig. 2.** TFE content dependence of  $T_m$  of vinylidene fluoride – TFE random copolymers in comparison with that of ETFE copolymers.

of monomer should show further higher  $T_m$  as will be estimated in a later section.

In the TFE region below 50 mol% (region A), the  $T_m$  decreases linearly with decreasing TFE content, and approaches the melting point of polyethylene. In the region B or TFE 50–67 mol%, the melting point decreases also because the continuous E–TFE sequences are partially blocked by an invasion of an excess of TFE units,  $-(E-TFE)_n-TFE-(E-TFE)_m-$ . In the region C or TFE > 67 mol%, the molar fraction of TFE segment is furthermore larger than that of E–TFE sequence. The relative amount of longer TFE sequences increase and the  $T_m$  approaches almost linearly the melting point of PTFE homopolymer. According to the X-ray diffraction study [15], some contribution of PTFE helical segments can be detected in the X-ray diffraction pattern expected to the E/TFE copolymers with the planar zigzag conformation, suggesting that the zigzag and helical sequences coexist along the molecular chain. An increase of such a PTFE helical sequence might result in the increase of melting point as seen in Figs. 1 and 2. The common behavior of melting point observed for ETFE and VDF/TFE copolymers in the TFE region higher than 70 mol% may come from such a structural characteristic that the helical segmental part increases its contribution in the crystal lattice, although the details are not known well.

As pointed out above, the TFE 50 copolymer shows the highest melting temperature. Here we try to clarify the relationship between the melting point and the ETFE alternating sequence by taking into account the statistical array of E and TFE monomeric units. If we assume an ideal copolymerization reaction for this system, then the E–E, TFE–TFE and E–TFE sequential ratios are calculated as shown in Fig. 3. In this calculation, the monomer reactivity ratios  $r_1$  and  $r_2$  were assumed to be 0.06 and 0.14, respectively, where TFE is monomer 1 and E is monomer 2 [23]. These values were obtained by analyzing the actually-observed relationship of monomer ratios between the starting mixture of E and TFE monomers and the synthesized polymers and showed a good agreement with the values reported in reference [3]. Using these values of  $r_1$  and  $r_2$ , the maximal alternating sequential fraction is calculated to be 0.92 for 50 mol% TFE content.

Fig. 4 shows the dependence of  $T_m$  on the alternating sequential fraction (TFE–E) in the B region indicated in Fig. 1. The  $T_m$  changes almost linearly with the alternating sequential fraction. The melting point of the perfectly alternating hypothetical copolymer

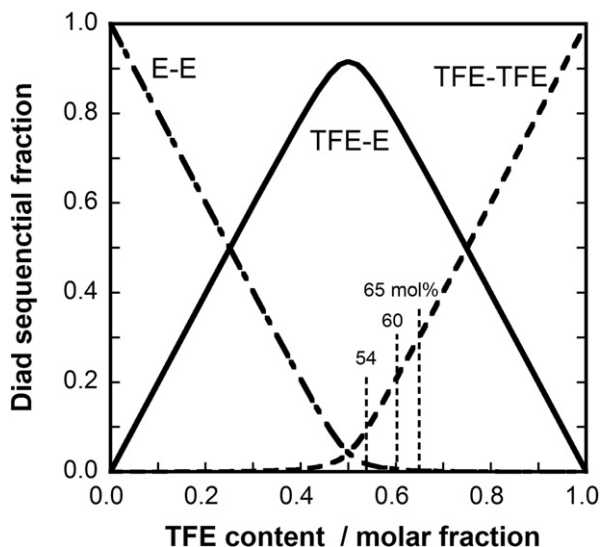


Fig. 3. Diad sequential distribution (E–E, TFE–TFE and E–TFE) calculated for ETFE copolymers, where the monomer reactivity ratios  $r_1 = 0.06$  and  $r_2 = 0.14$  were used (TFE: the monomer 1, and E: the monomer 2).

( $T_m^0$ ) may be estimated to be 293 °C by extrapolating the alternating sequential fraction to 1.

It may be possible to assume that the copolymer in the region B is approximately a random copolymer of the alternating E–TFE monomer units and TFE monomer units,  $-(E-TFE)_{1-x}-(TFE)_x-$ . The monomer reactivity ratios of such hypothetical copolymers can be calculated as a function of monomer composition (mole fraction): the calculated monomer reactivity ratios  $R_1$  and  $R_2$  are 15 and 0.07, respectively, where the hypothetical E–TFE monomer is monomer 1 and TFE monomer is monomer 2 (see Appendix).

The melting point behavior shown in Fig. 4 may be interpreted on the basis of a modified Flory's equation concerning the melting point of random copolymers. The Flory's theory originally assumed that only the monomer units of the same type are included in the crystal lattice and the comonomer units are excluded from the lattice [26]. Eby derived the equation of  $T_m$  for a copolymer in which both of the comonomers are included in the crystal lattice

[27]. The equation derived by Eby is essentially the same as the Flory's equation although the starting assumptions were different from each other. The melting temperature of the perfectly alternating copolymer ( $T_m^{\text{perfect}}$ ) is given by eq. (1).

$$1/T_m = 1/T_m^{\text{perfect}} - \alpha \cdot X \quad (1)$$

where  $X$  is a molar ratio of comonomer or TFE and  $T_m^{\text{perfect}}$  is the melting temperature of an perfectly alternating copolymer. The coefficient  $\alpha$  is a constant. In the numerical calculation of eq. (1), the melting points of the melt-cooled samples with different E/TFE contents were applied to the  $T_m$  in eq. (1). Fig. 5 shows the plot of  $1/T_m$  against  $X$  for the copolymers included in the region B. The  $T_m^{\text{perfect}}$  is evaluated to be 295 °C by extrapolating to  $X = 0$  or for the perfectly alternating copolymer. The value is close to the extrapolated value 293 °C shown in Fig. 4.

### 3.2. Glass transition temperature

The behavior of  $T_g$  is also unique for these ETFE copolymers. The maximal  $T_g$  is detected for the 50 mol% TFE copolymer. The  $T_g$ 's of the copolymers included in the region B (Fig. 1) is plotted against the alternating sequential fractions as shown in Fig. 6. An extrapolation to the perfect alternating fraction 1.0 gives the  $T_g$  of 145 °C.

The equation of  $T_g$  for a copolymer was proposed by Gibbs and Dimazio [28] at first and modified by Uematsu [29] as given in eq. (2).

$$T_g = f_{aa}T_g^a + f_{bb}T_g^b + f_{ab}T_g^{ab} \quad (2)$$

The  $f_{aa}$ ,  $f_{bb}$  and  $f_{ab}$  are, respectively, the diad sequential ratios of aa, bb and ab monomer sequences. The  $T_g^a$ ,  $T_g^b$  and  $T_g^{ab}$  are the glass transition points of E–E–E, TFE–TFE–TFE and TFE–E–TFE respectively. The  $T_g$  of E unit is assumed to be that of polyethylene,  $-128$  °C as generally accepted [30]. The  $T_g$  of TFE unit is assumed to be  $-9$  °C, as calculated by Wall [21]. By substituting the  $f_{aa}$ ,  $f_{bb}$  and  $f_{ab}$  values estimated from Fig. 3, the  $T_g^{ab}$  or the  $T_g$  of perfectly alternating copolymer of E and TFE is estimated to be  $145 \pm 5$  °C, which is almost equal to the extrapolated value 145 °C obtained in Fig. 6.

It should be noticed here that the  $T_g$  of the perfectly alternating hypothetical copolymer is higher than that of PTFE, suggesting that the micro-Brownian motion of the perfectly alternating copolymer

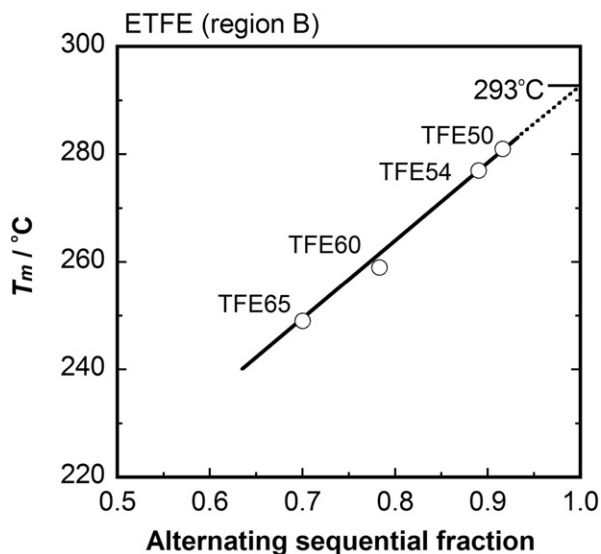


Fig. 4. Dependence of  $T_m$  on the alternating sequential fraction estimated for ETFE copolymers in the region B.

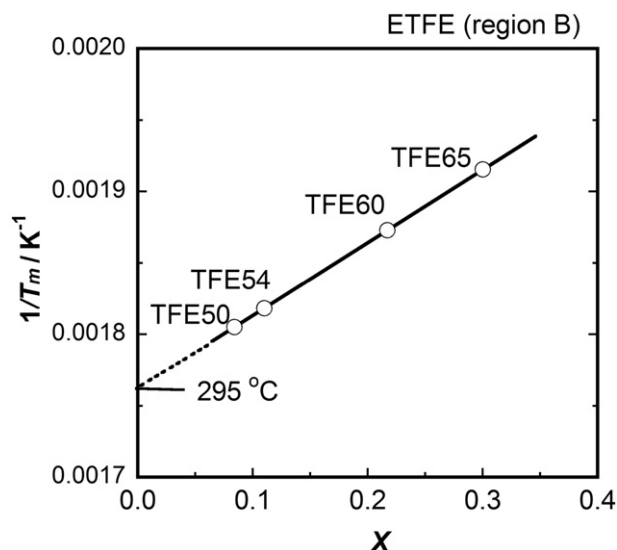


Fig. 5. Dependence of  $1/T_m$  on the molar content of TFE unit ( $X$ ) observed for ETFE copolymers in the region B.

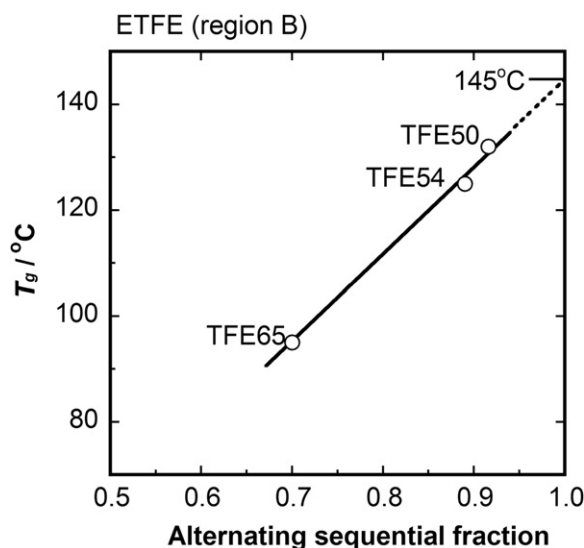


Fig. 6. Dependence of  $T_g$  on the alternating sequential fraction estimated for ETFE copolymers in the region B.

chain is more difficult to occur than the case of PTFE chain because of higher torsional energy barrier of the copolymer chain [31]. On the other hand, the observation of minimal  $T_g$  point at around 70 mol% TFE content may originate from the crossover of decreasing tendency of  $T_g$  in the region B and the increasing tendency of  $T_g$  in the region C due to the increment of long TFE segments. The torsional barrier around the TFE–TFE sequence is lower than that around the E–TFE segments, resulting in the decrement of  $T_g$  with an increase of TFE content in the region B. On the other hand PTFE itself is easy to take a helical conformation even in the amorphous region, increasing the hardness of random coil and increasing the  $T_g$  of the copolymer with higher TFE content in the region C. As a result the minimal  $T_g$  point is obtained between regions B and C. These microscopic discussions are needed to be checked by a computer simulation method.

#### 4. Conclusions

The TFE content dependence of  $T_m$  and  $T_g$  of ETFE shows unique behavior with the maximal and minimal points. The  $T_m$  may be classified into three regions of the different characters as shown in Fig. 1.

The existence of the maximal  $T_m$  at 50 mol% TFE can be interpreted by presuming the perfectly alternating hypothetical copolymer. The  $T_m$  of perfectly alternating copolymer is estimated to be 295 °C by performing the extrapolation to the perfectly alternating ratio. This value is supported reasonably by utilizing the modified Flory's equation as derived by Eby.

On the other hand, the existence of minimal  $T_m$  at around 70 mol% TFE content is considered to come from the difference in chain conformation between the regions B and C. The copolymer in the region B may be assumed to be a copolymer consisting of hypothetical E–TFE units and TFE units. The copolymer in the region C includes the long TFE segments of helical conformation, as evidenced by the X-ray diffraction data. The  $T_m$  increases gradually with an increment of TFE units. Similarly the maximal  $T_g$  was reasonably interpreted on the basis of the modified Gibbs–Dimazio's equation. The  $T_g$  extrapolated to the perfectly alternating copolymer was estimated to be 145 °C.

In this way, the  $T_m$  and  $T_g$  of ETFE are remarkably influenced by the degree of alternation of E and TFE monomeric units along the skeletal chains. As mentioned in the introduction, there are several kinds of fluorine copolymers which show the characteristic thermal

behaviors similar to that of ETFE copolymer. For example, IB–TFE copolymer and propylene–TFE copolymer show the maximal  $T_m$  and  $T_g$  at about 50 mol% TFE monomer content [21]. These observations may be also reasonably interpreted in a similar way to the discussion made in the present paper.

#### Acknowledgment

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#### Appendix. Monomer reactivity ratios of hypothetical E–TFE/TFE copolymer

ETFE copolymer included in the region B is assumed to be a random copolymer of the statistical distribution of E–TFE (1) and TFE (2) monomer units. Figure A below shows the molar fraction  $P$  (1) of monomeric unit 1 in the copolymer as a function of monomer 1 content  $M(1)$  in the starting mixture of monomers 1 and 2. These monomer reactivity ratios  $r_1$  and  $r_2$  are calculated to be 15 and 0.07 respectively, indicating that this copolymer is a random copolymer.

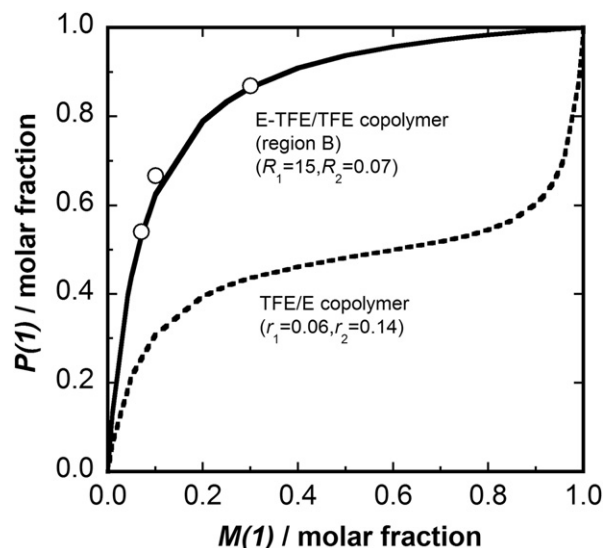


Fig. A. Molar fraction  $P(1)$  of monomer unit 1 in the copolymer plotted as a function of monomer 1 content  $M(1)$  in the starting monomer mixture. Copolymerization of TFE and E monomers: broken line, and that of hypothetical E–TFE and TFE monomers: solid line. Monomer reactivity ratios are  $r_1 = 0.06$  and  $r_2 = 0.14$ , and  $R_1 = 15$  and  $R_2 = 0.07$ , respectively.

These reactivity ratios can be also estimated as derived in the following way.

Copolymerization reaction consists of four propagating steps. For example, in the case of copolymerization of TFE monomer (T) and E monomer (E),

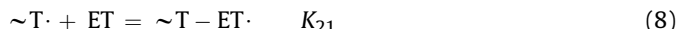
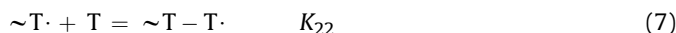
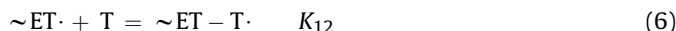
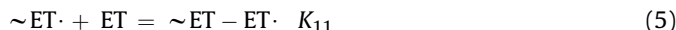


where  $\sim T\cdot$  is the TFE end group of the copolymer and  $\sim E\cdot$  is the E end group.  $k_{ij}$  is the rate constant of the copolymerization reaction between the two monomers.

The monomer reactivity ratios are expressed as below.

$$r_1 = k_{11}/k_{12} = 0.06 \text{ and } r_2 = k_{22}/k_{21} = 0.14$$

Similarly, in the case of copolymerization of the E–TFE (ET) and TFE (T) monomeric units, the following reactions are considered to occur hypothetically.



where  $\sim\text{ET}\cdot$  is the ET end group of the copolymer and  $\sim\text{ET}-\text{ET}\cdot$  is the ET dyad end group.  $K_{ij}$  is the rate constant of the copolymerization reaction between the two monomers.

Since eqs (5) and (8) correspond to eq. (2) and eqs. (6) and (7) correspond to eq. (1), respectively, then we have the following relations, if the penultimate effect can be neglected in this copolymerization reaction.

$$R_1 = K_{11}/K_{12} = k_{12}/k_{11} = 1/r_1 = 1/0.06 = 16.7 \text{ and}$$

$$R_2 = K_{22}/K_{21} = k_{11}/k_{12} = r_1 = 0.06$$

These values are almost equal to the calculated values:  $R_1 = 15$  and  $R_2 = 0.07$ .

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