

Study of Radical Copolymerization of Tetrafluoroethylene with Ethylene in Bulk

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SYNOPSIS

Radical copolymerization of tetrafluoroethylene (TFE) with ethylene (E) by azo-*bis*-isobutyronitrile in the temperature interval 333–363 K, monomer pressure from 3.0 to 7.0 MPa at TFE/E molar ratio from 77/23 to 23/77 in bulk was carried out. The effect of reaction conditions on the yield, molecular weight, and polymer composition of copolymer synthesized was studied. White powdery alternating copolymers were obtained at TFE content in the monomer mixture from 65 to 85 mol %. Copolymerization rate R was described by the equation $R = k_M[\ln][\sum M]^{1.3}$ which was related to the heterophase character of the reaction. The reactivity ratio of TFE and E (0.067 ± 0.12 and 0.52 ± 0.18 , respectively) and apparent activation energy $E_a = 135$ kJ/mol were found. The TFE and E block formation probabilities were calculated and compared with IR spectroscopy data. Melting point, entropy, and enthalpy of fusion of the entirely alternating copolymers were determined. Some of the basic properties of the alternating copolymers obtained were also studied. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The pioneer efforts to obtain melt-processable fluorocontaining polymers are connected with copolymerization of tetrafluoroethylene (TFE) with ethylene (E) at high pressure in the presence of organic peroxides.^{1–3}

In the 1960s Tabata et al. started systematic research on radiation-induced copolymerization of TFE with 1-alkenes, such as ethylene,⁴ propylene,⁵ and isobutylene.⁶ They studied the copolymerization of TFE with E in liquid phase under ionizing radiation at temperature of 195 K. The authors found that the reaction rate abruptly decreases with the increase of E content in the monomer mixture. A radical mechanism of copolymerization was suggested and, by infrared (IR) spectroscopy, the statistical character of the distribution of monomer units in TFE-E copolymer was proved. The authors⁷ calculated the gas-phase reactivity ratio to be $r_E = 0.01$ and $r_{TFE} = 0.1$.

Sorokin et al.^{8,9} studied the reactivity of TFE and E at 273 K and γ -rays dose rate of 10 rad/s. The relative reactivity ratios were reported to be $r_{TFE} = 0.04$ and $r_E = 0.12$, and $Q-e$ parameters for TFE 0.047 and 1.95, respectively.

In radiation liquid-phase copolymerization of TFE with E, Galperin et al.¹⁰ found similar values for reactivity ratios and proved that the copolymerization rate is proportional to the dose rate by power of $n = 0.6$ – 0.7 . Authors¹⁰ attributed the deviation of n from 0.5 to the heterogeneous mechanism of copolymerization, since the copolymer obtained was insoluble in the reaction medium.

Aiming to limit the heterophaseity in the initial stage, Kabankin et al.¹¹ carried out photochemically initiated copolymerization of TFE with E at low pressure (vacuum). Under these conditions, the calculated reactivity ratios were found to be $r_E = 0.38$ – 0.46 and $r_{TFE} = 0.10$ – 0.25 .

While radiation-induced copolymerization of TFE with E in bulk is well studied, results for chemically initiated copolymerization in bulk has not been reported.

The aim of this work is to study chemically initiated copolymerization of TFE with E in gas phase. The influence of polymerization conditions and

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monomer composition on the reaction kinetics and copolymerization composition are also discussed.

EXPERIMENTAL

Materials

Tetrafluoroethylene (99.5% purity) was obtained by debromination of 1,2-dibromotetrafluoroethane.¹²

Ethylene (commercial product of Neftochim Co., Bulgaria, 99.9% purity) was used without further purification. Initiators *tert*-butyl peroxybenzoate, di-benzoyl peroxide, di-cetyl peroxydicarbonate, azo-*bis*-isobutyronitrile (AIBN) were commercial products of Akzo Chemie.¹³

Copolymerization Procedure

Copolymerization of TFE with E was carried out in stainless steel autoclave of 500 cm³, equipped with pressure gauges and safety valves. Oxygen in the monomer was removed by freeze-thaw technique at 10⁻³-10⁻⁴ mm Hg.

The synthesis of the copolymers was carried out at inhibitor concentrations [AIBN] from 0.1 to 1.5 wt % vs. initial monomer mixture. Reaction temperature was from 333 to 363 K, pressure from 3.0 to 7.0 MPa, copolymerization time up to 24 h and mole ratio of TFE/E from 23/77 to 77/23.

Polymerization products were washed with methanol and dried under vacuum at 343 K to constant weight.

Physicochemical Analyses

The compositions of TFE-E copolymers obtained were determined by elemental analysis of carbon and hydrogen by using automatic analyzer model 1104 (Carlo Erba, Italy) and of fluorine, determined by the fluorine anions' content measured by ion-selective electrode (Kritur, Czech Republic).

Molecular weight was assessed by the melt index (MI) (573 ± 1 K, load 105 N). IR spectra of copolymer films (thickness below 100 μm) were taken on a spectrophotometer Specord-M80 (Carl Zeiss, Germany). The distribution of monomer units was determined by the ratio of absorptions at 773 cm⁻¹ [$\rho(\text{CH}_2-\text{CH}_2)_{n=1}$ sequences], 733 cm⁻¹ [$\rho(\text{CH}_2-\text{CH}_2)_{n=2}$ sequences], and 721 cm⁻¹ [$\rho(\text{CH}_2-\text{CH}_2)_{n\geq 3}$ sequences] bands vs. the absorption at 2973 cm⁻¹ (valent asymmetric oscillations of $\nu_{\text{as}}(\text{CH}_2)$) by a technique described earlier.¹⁴

The initial temperature of thermooxidative destruction (T_d) of the copolymers was measured by differential thermal analysis (DTA) on a derivatograph OD-102 (MOM, Hungary) at a heating rate 10 K/min in air. The melting temperature (T_m) of the copolymers was determined by using a differential scanning calorimeter DSC-111 (Setaram, France) at a scanning rate 10 K/min in air.

The copolymers were kept for 5 h at 548 ± 5 K to calculate their thermostability from the weight loss (%). The copolymer density was determined picnometrically in distilled water at 293 K.

The tensile characteristics were measured by a testing machine of Zwick, Germany, and the dielectric properties by instruments of TESLA, Czech Republic.

The chemical resistivity of the copolymers was determined according to ASTM D543.

RESULTS AND THEIR DISCUSSION

Copolymerization of TFE with E was carried out in bulk with several initiators: *tert*-butyl peroxybenzoate, di-benzoyl peroxide, di-cetyl peroxydicarbonate, azo-*bis*-isobutyronitrile (Table I). White powdery plastics with various dispersities were obtained. The copolymerization rate (R) was calculated from the initial slope of the yield-time kinetic curves. It

Table I Copolymerization of TFE with E in Bulk in Presence of Different Initiators^a

No.	Initiator	[In], mol %	R , %/h	MI, g/10 min	T_m , K	T_d , K	ΔT , ^b K	Wt. Loss, %
1	<i>tert</i> -butylperbenzoate	0.39	1.7	5.8	538	593	55	0.8
2	Di-benzoyl peroxide	0.33	1.2	4.9	535	600	65	0.6
3	Di-cetylperoxodicarbonate	0.13	0.9	5.6	530	603	73	1.1
4	Azo- <i>bis</i> -isobutyronitrile	0.46	2.8	3.3	533	618	85	0.4

^a Polymer conditions: $T = 343$ K, $P = 4.5$ MPa, molar ratio TFE/E of 70/30.

^b $\Delta T = T_d - T_m$.

can be seen from the analysis of some of their basic physical properties that copolymers with the best thermophysical and rheological characteristics were obtained with AIBN initiator.

With the exception of copolymerization of TFE with E in medium of chlorofluorocarbohydrates,¹⁵ no data has been reported on the use of azo-compounds as initiators of this synthesis. Azo-compounds, in particular azo-nitriles, are more suitable than organic peroxides because induced decomposition does not occur (therefore the chain transfer constant is low), decomposition of first order proceeds at constant rate in various solvents and side reactions (including crosslinking and grafting)¹⁶ does not take place. This is why polymers obtained with this initiator possessed the highest molecular weight (low MI) and stable end groups, which improved their properties (Table I).

Taking this into account, the following experiments were carried out with AIBN initiator.

The dependence of copolymer yield (Y) on copolymerization time at various initiator concentrations $[In]$ is shown in Figure 1. The kinetic curves show that the copolymerization of TFE with E proceeds with an induction period and during the first several hours in stationary state. The induction period decreases with the increase of $[In]$ and changes in the range from 5 to 25 min.

The effect of $[In]$ on the copolymerization rate (R) and MI of the copolymers obtained is shown in logarithmic coordinates in Figure 2. Obviously, R

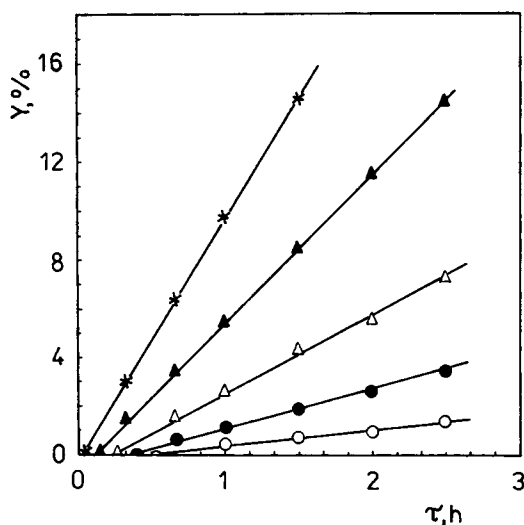


Figure 1 Kinetic curves of copolymerization of TFE with E at different initiator concentrations (wt %): (○) 0.1, (●) 0.25, (△) 0.50, (▲) 1.00, (*) 1.50. Polymerization conditions: 5.0 MPa, 343 K, molar ratio TFE/E of 70/30.

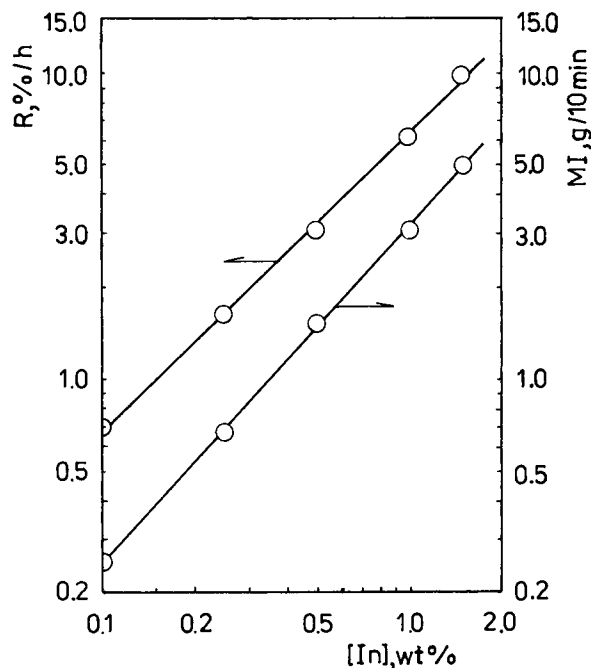


Figure 2 Dependence of copolymerization rate (R) and melt index (MI) on initiator concentration $[In]$. Polymerization conditions as in Figure 1.

increases and molecular weight decreases with the increase of $[In]$.

It is well known for radical copolymerization that the reaction order by $[In]$ is 0.5, due to bimolecular chain termination.¹⁷ Under the conditions studied, the dependence of R on AIBN concentration was found to be

$$R \propto [In]^{1.0} \quad (1)$$

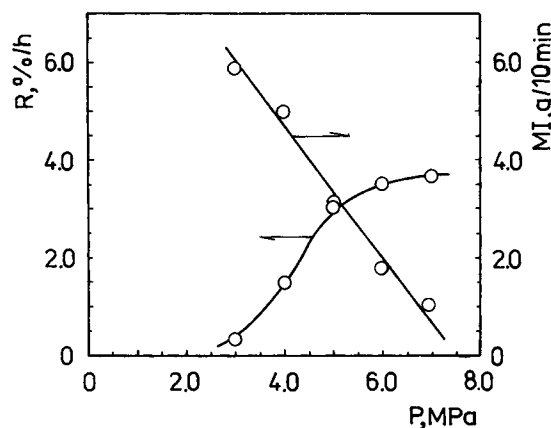


Figure 3 Dependence of copolymerization rate (R) and melt index (MI) on reaction pressure (P). Polymerization conditions: 343 K, $[In] = 0.50$ wt %, molar ratio TFE/E of 70/30.

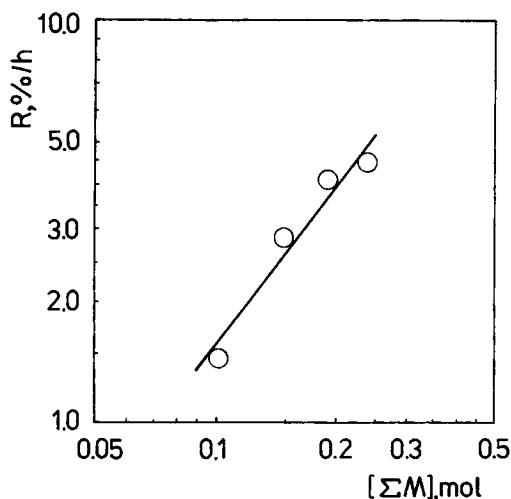


Figure 4 Dependence of copolymerization rate (R) on total monomer content (ΣM). Polymerization conditions: 7.0 MPa, 343 K, $[\text{In}] = 0.50$ wt %; molar ratio TFE/E of 70/30.

The deviation of the power from the value of 0.5 is connected with the heterophase character of the process, since the copolymer obtained is insoluble in the reaction medium and exerts autocatalytic influence.¹⁸ From the point of view of the copolymerization rate and molecular weight, a reasonable compromise was reached at AIBN concentration of 0.5 wt %.

The effect of the reaction pressure (from 3.0 to 7.0 MPa) on R and copolymer molecular weight was studied (Fig. 3). The reaction rate and molecular weight increase with pressure. TFE and E are gaseous monomers and the increase of the pressure conduces higher monomer concentration in reaction medium. The following series of experiments were carried out at 7.0 MPa.

The influence of the total monomer content (ΣM) on R is shown in Figure 4, where the reaction order by ΣM is 1.3. The higher order by monomers can be attributed to their participation in the chain initiation, which was proved by other authors.¹⁹

The common initial stationary copolymerization rate can be described by Eq. (2):

$$R = k_M [\text{In}]^{1.0} [\Sigma M]^{1.3} \quad (2)$$

The effect of monomer composition on R is shown in Figure 5. Obviously, R increases ca. 8 times with the increase of TFE content in the monomer mixture, with maximum values reached at [TFE] over 70 mol % in the monomer mixture.

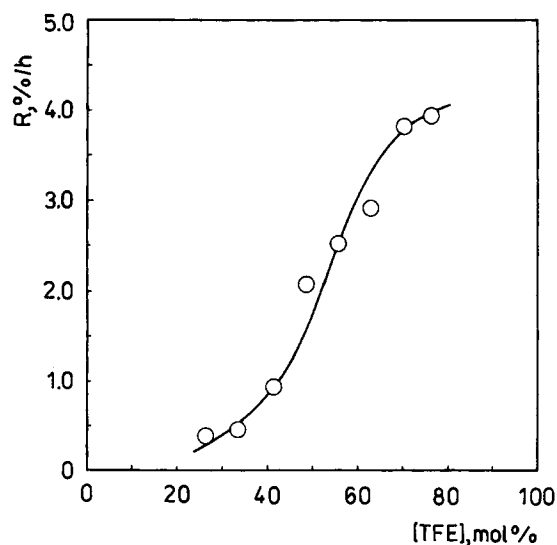


Figure 5 Dependence of copolymerization rate (R) on TFE content in monomer mixture. Polymerization conditions: 7.0 MPa, 343 K, $[\text{In}] = 0.50$ wt %.

Series of experiments were carried out at different mole ratios of the monomers and conversion up to 15% to reveal the dependence polymer-monomer composition. The reactivity ratios calculated by the nonlinear least-square method of Tidwell and Mortimer²⁰ were found to be

$$r_{\text{TFE}} = 0.067 \pm 0.12 \quad \text{and} \quad r_{\text{E}} = 0.52 \pm 0.18$$

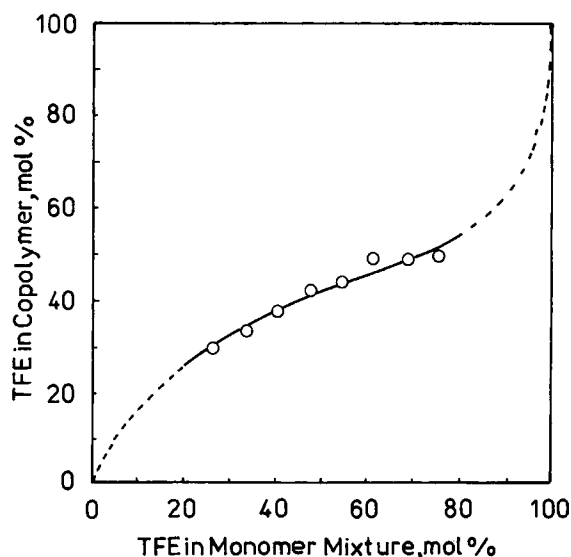


Figure 6 Composition curve of C_2F_4 — C_2H_4 copolymerization. Polymerization conditions: 7.0 MPa, 343 K, $[\text{In}] = 0.50$ wt %.

Table II E Block Sequences of TFE-E Copolymers from IR Spectroscopy Data

Initial Monomer Mixture TFE/E, Mol %	$\log I_0/I_{773} (n = 1)$	$\log I_0/I_{733} (n = 2)$	$\log I_0/I_{721} (n \geq 3)$
	$\log I_0/I_{2973}$	$\log I_0/I_{2973}$	$\log I_0/I_{2973}$
77/23	0.20	0.04	0.01
70/30	0.23	0.08	0.01
63/37	0.22	0.11	0.04
49/51	0.21	0.22	0.04
35/65	0.23	0.41	0.09

The copolymer-monomer composition curve, according to the reactivity ratio calculated, as well as the experimental points, are shown in Figure 6. Formation of azeotropic copolymer was observed at 36 mol % TFE content in the initial monomer mixture (Fig. 6).

The product of the reactivity ratios (0.0348) shows a tendency to formation of alternating copolymer, expressed most clearly for TFE content in the initial monomer mixture from 65 to 80 mol %.

Taking into account the reactivity ratios obtained and known values of Q - e parameters for E (0.015 and -0.200)²¹ according to the Alfrey and Price equation, Q - e parameters for TFE were calculated to be 0.020 and 1.630. These values are close to those reported earlier.²¹

Using the formulas of Wall²² and Medvedev²³ and the values of r_{TFE} and r_E , the intramolecular distribution of monomer units in the macromolecule was calculated.

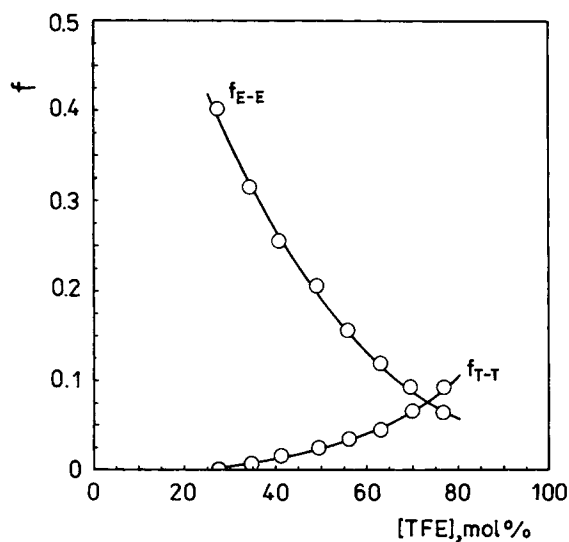


Figure 7 Dependence of probabilities for formation of TFE (f_{T-T}) and E (f_{E-E}) blocks on TFE content in initial monomer mixture.

The probabilities of block formation of TFE (f_{T-T}) and E (f_{E-E}) depending on TFE content in the initial mixture are shown in Figure 7. The least probability of formation of E and TFE blocks corresponds to 70–75 mol % TFE content. These results were proved by the data obtained by IR spectroscopy (Fig. 8) for E blocks, shown in Table II.

These data correlate well with the distribution functions²⁴ F_T and F_E (content in mol %) of TFE and E units in macromolecule chain, composed of i monomer units (Table III).

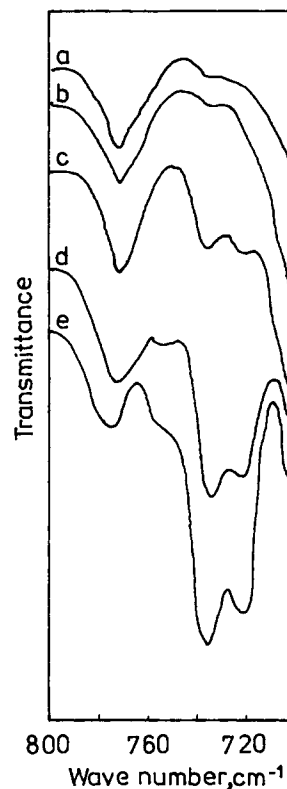


Figure 8 Infrared spectra of TFE-E copolymer in the range of 700–800 cm^{-1} at initial monomer mixtures TFE/E (mol %): (a) 77/23, (b) 70/30, (c) 63/37, (d) 49/51, (e) 35/65.

Table III Distribution Functions F_{M_i} of Monomer Sequences in TFE-E Copolymer at TFE/E Molar Ratio of 70/30

$\text{-(C}_2\text{F}_4\text{)}_i$	F $\text{-(C}_2\text{F}_4\text{)}_i$, Mol %	$\text{-(C}_2\text{H}_4\text{)}_i$	F $\text{-(C}_2\text{F}_4\text{)}_i$, Mol %
$\text{-(C}_2\text{F}_4\text{)}$	36.36	$\text{-(C}_2\text{H}_4\text{)}$	34.38
$\text{-(C}_2\text{F}_4\text{)}_2$	9.81	$\text{-(C}_2\text{H}_4\text{)}_2$	12.53
$\text{-(C}_2\text{F}_4\text{)}_3$	1.98	$\text{-(C}_2\text{H}_4\text{)}_3$	3.42
$\text{-(C}_2\text{F}_4\text{)}_4$	0.43	$\text{-(C}_2\text{H}_4\text{)}_4$	1.08
	48.59		51.41

The melting temperatures of TFE-E copolymers decrease with the increase of E content in the copolymer from 50.5 to 70.6 mol % (Fig. 9). This relationship can be described by the Flory equation²⁵ for statistical copolymers:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln X_A \quad (3)$$

where X_A = mole content of alternating sequence
 $\text{-(CH}_2\text{-CH}_2\text{-CF}_2\text{-CF}_2\text{-)}$

T_m^0 = equilibrium melting temperature of ideal polymer with constitution repeated unit
 $\text{-(CH}_2\text{-CH}_2\text{-CF}_2\text{CF}_2\text{-)}$

T_m = melting temperature of copolymer, where E units are in excess vs. 1 : 1 TFE/E mole ratio

The enthalpy (ΔH_u) and the entropy (ΔS_u) of the copolymer for $\text{(CF}_2\text{-CF}_2\text{-CH}_2\text{-CH}_2\text{-)}$ repeated sequences are calculated from the slope of the straight line, describing the above dependence (Fig. 9).

The thermodynamic values for entirely alternating copolymer, together with the corresponding values for homopolymers polyethylene (PE)²⁶ and

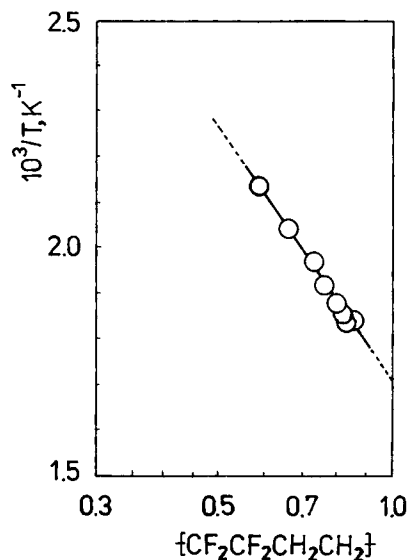


Figure 9 Plot of $1/T_m$ against molar content of $\text{(CH}_2\text{-CH}_2\text{-CF}_2\text{-CF}_2\text{-)}$ units for TFE-E copolymers. Polymerization conditions as in Figure 5.

poly(tetrafluoroethylene) (PTFE)²⁷ are shown in Table IV. Since poly(vinylidene fluoride) (PVDF)²⁸ can be examined as an isomer of TFE-E copolymer, data for PVDF are also included in the table for comparison.

The equilibrium melting temperature determined for an ideal alternating copolymer is between those of PE and PTFE and is close to that cited by other authors.²⁹ In Table IV $\Delta H_u/M_0$ (where M_0 is molecular weight of an alternating unit) and $\Delta S/\text{bond}$ for TFE-E are also given and they show intermittent values.

The total activation energy of copolymerization of TFE with E (135 kJ/mol) was calculated from the dependence R/T in the Arrhenius coordinates (Fig. 10). The high value of the total apparent activation energy of thermochemical initiation at heterophase copolymerization is due to the increased value of the order by $[\ln]$ ($n = 1$), compared to the single-phase polymerization ($n = 0.5$).

Table IV Thermodynamic Quantities

Polymer	T_m^0 , K	ΔH_u , J/Mol	$\Delta H_u/M_0$, J/g	ΔS_u , J/Deg Mol ⁻¹	$\Delta S_u/\text{Bond}$ J/Deg
Polyethylene	410.5	4010	286	9.76	9.76
Poly(tetrafluoroethylene)	600.0	5730	57.3	9.55	4.78
Poly(vinylidene fluoride)	443.0	6690	105.0	15.10	7.55
$\text{-(C}_2\text{F}_4\text{-C}_2\text{H}_4\text{-)}_n^a$	583.0	12 370	96.6	21.22	5.30

^a This work.

Table V Physical Properties of TFE-E Copolymer^a

No.	Properties		Testing Method, ASTM
1.	Density, kg/m ³	1700–1750	
2.	Melt index, g/10 min	1.6–1.9	
3.	Melting temperature, K	543	
4.	Decomposition temperature, K	633	
5.	Thermostability by weight loss, %	0.3	
6.	Tensile strength, MPa	25–30	D638
7.	Elongation at break, %	130–200	D638
8.	Dielectric properties:		
	Dielectric constant at 1 MHz	2.20	D150
	Volume resistivity, Ω cm	1.5 × 10 ¹⁶	D150
	Dissipation factor at 1 MHz	0.012	D150
	Dielectric strength (2 mm thickness), kV/mm	20	D149

^a Polymerization conditions: [AIBN] = 0.50 wt %, $T = 343$ K, $P = 7.0$ MPa, TFE/E molar ratio of 70/30, copolymerization time 6 h.

MI increases from 0.6 to 41.5 g/10 min in the range from 333 to 363 K (molecular weight decreases) due to the high initiation rate together with the increase of the chain termination rate.

For the determination of the dependence between average molecular weight (\bar{M}_n) and melt index (MI), the following equation was used³⁰:

$$\eta_0 = k\bar{M}_n^{3.4} \quad (4)$$

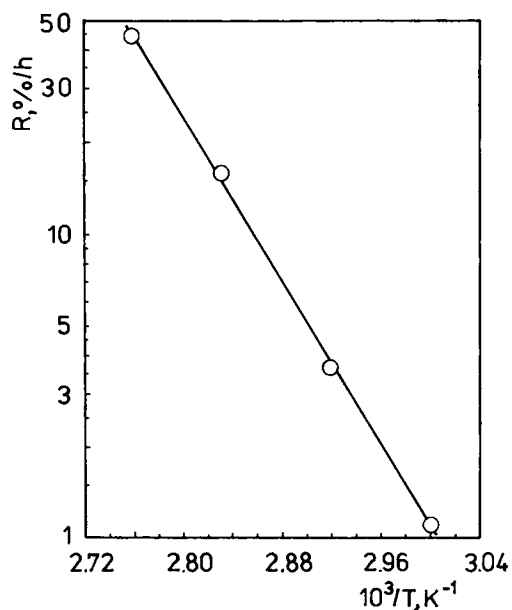


Figure 10 Dependence of copolymerization rate (R) on temperature (T) in Arrhenius coordinates. Polymerization conditions: 7.0 MPa, [In] = 0.50 wt %; molar ratio TFE/E of 70/30.

where η_0 is initial Newtonian viscosity, $k = 3.19 \times 10^{-13}$ Pa s.

For TFE-E melts η_0 was measured by rotational RV2 Searle type HAAKE viscometer (Germany) by a method described in our earlier work.³¹ On this basis, the dependence of MI on \bar{M}_n was found to be

$$MI = 3 \times 10^{27} \bar{M}_n^{-5.5} \quad (5)$$

From the studies carried out it can be concluded that copolymer with best yield, good rheological and thermophysical characteristics was obtained at a pressure of 7.0 MPa, 343 K, 0.50 mass % AIBN initiator, TFE/E molar ratio of 70/30 and 6 h copolymerization time.

Some of the basic physical properties of the copolymers synthesized are given in Table V.

TFE-E is inert to strong mineral acids, inorganic bases, halogens, carboxylic acids, aromatic and aliphatic hydrocarbons, alcohols, aldehydes, ketones, etc. (weight gain < 1.5%).

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