Study of Radical Copolymerization of Tetrafluoroethylene with Ethylene in Suspension

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SYNOPSIS

Radical copolymerization of tetrafluoroethylene (TFE) with ethylene (E) was initiated by 2,2′-azo-bis-isobutyronitrile in batch and semibatch operation. The effect of reaction conditions (temperature, pressure, stirring speed, molar ratio of monomers, etc.) on copolymerization rate and copolymer molecular weight was studied. The highest reaction rate was observed at TFE content over 70 mol % and was found to be proportional to initiator concentration and total monomer content by powers of 0.9 and 1.54, respectively. These dependencies were attributed to the heterophase character of the copolymerization.

The monomer reactivity ratios and overall activation energy of the reaction were determined. The effect of the monomer composition on the distribution of monomer units in the copolymer chain was studied. Kinetic mechanism of the copolymerization was suggested.

Some of the basic physical properties and chemical resistance of the alternating copolymers synthesized were also determined. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The synthesis of fluoropolymers obeys the common principles of radical polymerization and, on the other hand, shows some special features of heterophase systems.[1] Namely, they are: auto-acceleration of the process in the initial stage, higher average rates and molecular weights of the polymers obtained, high values of the copolymerization activation energy,[2,3] etc.

In homogeneous reactions at low conversions, simple kinetic principles are usually observed: reaction rate is proportional to the square root of the initiator concentration and to the power of 1 of the monomer concentration.[4] Most of these principles can be disturbed if insoluble copolymer is obtained, which proves that the anomalous behavior is stipulated by the polymer separation in the course of the reaction.[5] Rather ample in this respect are the experiments of Abbere et al.[6] and Chapiro,[7] who studied the polymerization of styrene under homogeneous and inhomogeneous (in the presence of a condensing agent) conditions.

A few papers are dedicated to kinetic studies of emulsion and suspension copolymerization of tetrafluoroethylene (TFE) with ethylene (E). The difficulties are due to the insolubility of the copolymer in the reaction medium and to the absence of a correctly developed theory of copolymerization under inhomogeneous conditions. Water emulsion copolymerization of TFE with E has been carried out by Panshin et al.,[8] who calculated reactivity ratios of TFE and E in gaseous and water phases to be 0.05 ± 0.04 and 0.26 ± 0.08; 0.32 ± 0.09 and 0.03 ± 0.01, respectively. They also determined the probabilities for formation of TFE and E blocks by using the formulae of Wall[9] and Gindin et al.[10]

Modena et al.[11] studied emulsion and suspension copolymerization of TFE with E in presence of chlorofluoroethanes (freons) and calculated reactivity ratios by the nonlinear least-squares method.[12] They proved that these constants depend on the temperature: r_{TFE} = 0.045 ± 0.010 and r_E = 0.14 ± 0.03 at 338 K; r_{TFE} = 0.013 ± 0.008 and r_E = 0.10 ± 0.02 at 243 K. Yamabe et al.[13] carried out radiation-initiated copolymerization in aprotic solvents

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(freon R-113 and R-11) and found the following correlation between reaction rate (R) and irradiation dose (J): $R \propto J^{0.5-0.6}$ in R-113 and $R \propto J^{1.1}$ in R-11 medium. The reactivity ratios of TFE and E calculated by the Fineman–Ross[14] method are 0.22 and 0.32, respectively.

Among the methods reported in the literature[14-17] for determining the monomer reactivity ratios, the one suggested by Tidwell and Mortimer[12] gives the best results. The exact calculation of the reactivity ratios is substantial for the calculation of Q–e values. That is why, for a certain monomer, they vary rather widely.[18,19] One of the reasons for these differences is the heterophaseity of the copolymerization reactions, which requires comparison between reactivities of the different pairs of monomers under analogous conditions. On the other hand, the application of the nonlinear least-squares method for precise assessment of the relative reactivities of the monomers allows for better prediction of polymer structure and of its relationship with the properties of the copolymers synthesized.

Studies in recent years showed that the morphological structure of the polymer phase exerts significant influence on the copolymerization rate under heterogenization of the reaction medium.[20] Due to the separation of the polymer phase during copolymerization, a compositional inhomogeneity of the obtained copolymers appears, along with changes in their composition and in the intramolecular distribution of the comonomer units, compared with the homophase copolymerization.

In our previous work,[21] bulk copolymerization of TFE with E initiated with 2,2′-azo-bis-isobutyronitrile (AIBN) was studied. Alternating copolymers were obtained at TFE content in the initial monomer mixture from 65 to 80 mol %. The relative reactivity ratios of TFE and E were calculated to be $r_{TFE} = 0.067 \pm 0.12$ and $r_E = 0.52 \pm 0.18$, respectively, and apparent activation energy of the reaction was 135 kJ/mol. The overall copolymerization rate (R) is proportional to initiator concentration by power of unity and to total monomer concentration by power of 1.3. This is connected with the heterophaseity of the reaction in bulk.

The present paper is a continuation of our research and studies the effect of reaction conditions on the copolymerization of TFE with E in a water–alcohol medium, as well as the reaction kinetics. Some basic properties of the copolymers obtained are also discussed.

EXPERIMENTAL

Materials

Tetrafluoroethylene (99.5% purity) was obtained by debromination of 1,2-dibromotetrafluoroethane.[22]

Ethylene (commercial product of Neftochim Co., Bulgaria, 99.9% purity) was used without further purification. Initiator 2,2′-azo-bis-isobutyronitrile (98% concentration) was commercial product of Akzo Chemie, The Netherlands.[23]

Distilled water, *tert*-butanol (reagent grade) and methanol of guaranteed quality were also used.

Copolymerization Procedure

Copolymerization was carried out in batch (conversion up to 10%) and semibatch operation in a 300-cm^3 stainless-steel reactor (Buchi, Switzerland) equipped with cooling and heating jacket, magnetic coupled paddle-type agitator, safety rupture disk, and control panel. The reactor temperature was kept constant (± 0.1 K) by a thermostat and registered by a thermocouple. The reactor and the polymerization medium were connected to a pressure line and air was purged twice by evacuating and flashing with gaseous nitrogen; then the medium was introduced into the reactor. Oxygen was removed from TFE–E monomer mixture by the "freeze–thaw" technique (residual pressure 1–10 Pa). Under stirring, TFE and E were supplied to the rector in the necessary molar ratio. The copolymerization was carried out at given pressure, temperature, and stirring speed. The pressure was kept constant by continuous feeding of a TFE–E monomer mixture of molar ratio 50/50. Samples were taken from the reaction medium by a spherical valve at given time intervals. Series of experiments were carried out by this procedure under conditions and compositions shown in Table I. At the end of the copolymerization reaction the residual monomer gases were removed. The obtained product was then filtered and copolymers were washed twice with hot methanol and distilled water, dried under vacuum at 343 K, and weighed.

Measurements of Physical Properties of Copolymers

The copolymer compositions were determined by elemental analysis of carbon and hydrogen (measured by Erba Science 1108 analyzer, Italy) and fluorine (by ion-exchange chromatograph Dionex Serie 2000, USA).

Table I TFE–E Copolymerization Compositions and Conditions

No.	Components	Compositions							
		A	B	C	D	E	F	G	H
1	TFE–E ratio, mol %	75/25	75/25	Variable*	75/25	75/25	75/25	75/25	75/25
2	Monomer mixture, mol/L	6.0	6.0	6.0	Variable*	6.0	6.0	6.0	6.0
3	Water, g	100	100	100	Variable*	100	100	100	100
4	AIBN, mmol/L	Variable*	7.6	7.6	7.6	7.6	7.6	7.6	7.6
5	*tert*-BuOH, mol/L	5.3	5.3	5.3	5.3	5.3	5.3	Variable*	5.3
		Polymerization Conditions							
6	Pressure, MPa	4.2	4.2	4.2	4.2	Variable*	4.2	4.2	4.2
7	Temperature, K	338	338	338	338	338	Variable*	338	338
8	Stirring speed, s^{-1}	17.5	Variable*	17.5	17.5	17.5	17.5	17.5	17.5

* Notes: a: AIBN concentration from 3.8 to 10.3 mmol/L; b: Stirring speed from 11.6 to 20.0 s^{-1}; c: TFE–E molar ratio from 30/70 to 85/15 (batch operation); d: ΣM from 3.7 to 6.7 mol/L and water from 80 to 160 g; e: Pressure from 3.2 to 4.5 MPa; f: Temperature from 333 to 344 K; g: *Tert*-BuOH concentration from 2.6 to 5.3 mol/L.

The molecular weight was evaluated by the melt index (*MI*, 573 ± 1 K, load 105 N).

Infrared spectra of TFE-E copolymers were measured on 100-μm-thick films by a Specord-M80 spectrophotometer (Germany). The distribution of E units in the copolymer was determined by absorptions at 2973, 773, 733, and 721 cm^{-1} using a technique described by other authors.[24]

The initial temperature (T_d) and the activation energy (E_d) of thermooxidative decomposition of the copolymers were determined from differential thermal analysis (DTA) curves taken by a derivatograph OD-102 (Hungary) at a heat rate of 10 K/min in air. The melting temperature (T_m) of the copolymers was determined by differential scanning calorimeter DSC-111 (Setaram, France) at a heat rate of 10 K/min in air. The Vicat softening point was measured at 10 N load. The copolymer thermoaging was carried out at 573 ± 2 K for 1 h in air (static mode) and at five consecutive extrusions in an *MI* measuring gauge at 573 K and 105 N load (dynamic mode). The copolymer thermostability was determined by percent weight loss at 548 ± 5 K for 5 h.

The copolymer density was determined picnometrically in distilled water at 293 K.

The tensile characteristics were measure by a Zwick testing machine (Germany) and the dielectric properties by a Tesla instrument (Czech Republic).

The chemical resistivities of the copolymers was determined according to ASTM D 543.

Electron micrographs of copolymer suspensions were taken by a Tesla-BS340 scanning electron microscope (Czech Republic).

RESULTS AND DISCUSSION

It is well known that at high pressure TFE decomposes explosively to CF_4 and C. From this point of view the monomer mixture is much more dangerous, since the minimum energy for initiating explosion is one-third that required for TFE.[25] That is why the copolymerization of TFE with E must be strictly controlled for safety reasons. Even if the reaction is carried out at temperatures from 343 K to 373 K and pressures up to 3.0 MPa, this process is highly dangerous. Therefore, from an engineering point of view, copolymerization of TFE with E in a water–alcohol medium is of special interest, since it implies easier temperature control and the possibility of achieving high copolymerization rate and obtaining copolymers with better properties.

The initiator used during the development of the water-suspension method of copolymerization was AIBN, which stipulates higher thermostability of the copolymers obtained. It should be noted that the water-suspension copolymerization system used is of heterophase character and involves a number of variables: monomer's ratio in the initial monomer mixture, water/monomers ratio, temperature, pressure, etc. The kinetic principles are additionally complicated by the difference in monomers' solubility in the reaction medium, the different reactivities of TFE and E radicals and the variable dependence of copolymerization rate on the conversion.

Figure 1 shows the dependence of copolymer yield (Y) on initiator concentration [In] (Table I, composition A). Obviously, the reaction proceeds with

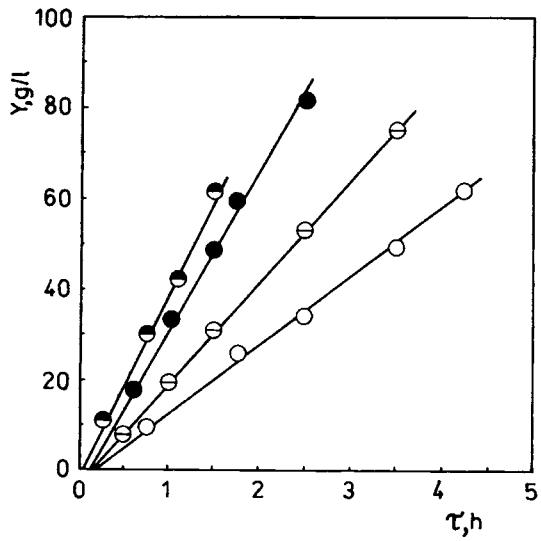

Figure 1 Kinetic curves of copolymerization of TFE–E at different initiator concentrations (mmol/l): ○, 3.8; ⊖, 5.8; ●, 7.6; ⊖, 10.3. Polymerization conditions as in Table I, composition A.

an induction period of 3 to 12 min and at a constant rate in the initial stage. The initial copolymerization rate (R) was determined from the slope of the yield/time curve. The effect of [In] on R and on the copolymers' MI and molecular weight, respectively is illustrated in logarithmic coordinates in Figure 2. The reaction order by [In] was found to be 0.9, which is significantly higher than that of the ordinary radical copolymerization (0.5). This can be attributed to the heterophase character of the process, since the copolymers obtained are insoluble in the reaction medium.

The values obtained for R are higher than those of bulk copolymerization,[21] due to the higher efficiency of AIBN in a water–alcohol medium ($f \approx 0.70$) than in solid phase ($f \approx 0.050$–0.035).[26] The decrease of the molecular weight with the increase of [In] is stipulated by the higher number of active centers and the higher possibility for their recombination. On this basis, a reasonable AIBN concentration of 7.6 mmol/L was selected for further experiments.

The effects of stirring speed (n) on the copolymerization rate and molecular weight of the copolymers obtained are shown in Table I, composition B (Fig. 3). This is an important factor because both monomers are slightly soluble in the reaction medium (solubility of E is 8×10^{-3} and TFE 1×10^{-3} mol/L). The reaction rate sharply increases with the stirring speed up to 15.2 s^{-1}; the copolymerization then proceeds in the kinetic region and further increase of the stirring speed showed no effect on R.

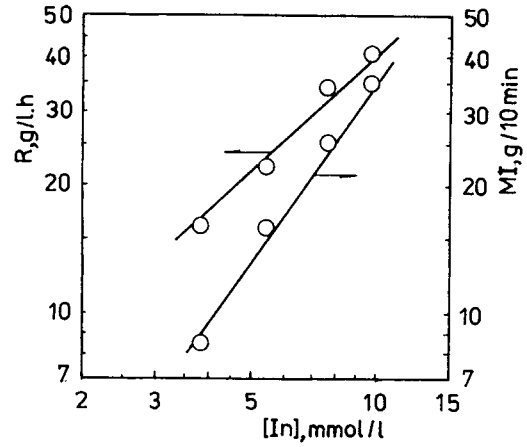

Figure 2 Dependence of copolymerization rate (R) and melt index (MI) on initiator concentration [In]. Polymerization conditions as in Figure 1.

This effect is rather complicated to be explained simply. In water-suspension polymerization of other monomers,[4] the role of the stirring speed has been analyzed; it has been suggested that the speed affected the interface between separate phases and the diffusion of monomers and other components from the medium, thus affecting R and MI.

Electron microscopic studies show that polymer particles detach as irregularly formed globules (Fig. 4). The particles' dimensions increase with the conversion from 3–12%. The detached polymer particles are not solid but have pores and cracks serving as channels for the diffusion of monomers into them. The morphologic characteristics of the detached polymer phase allow us to suggest that the particle's formation takes place at the expense of aggregations of small globules formed in the reaction medium.

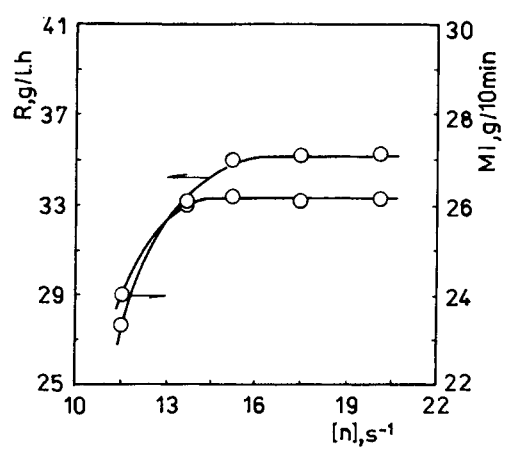

Figure 3 Dependence of copolymerization rate (R) and melt index (MI) on stirring speed (n). Polymerization conditions as in Table I, composition B.

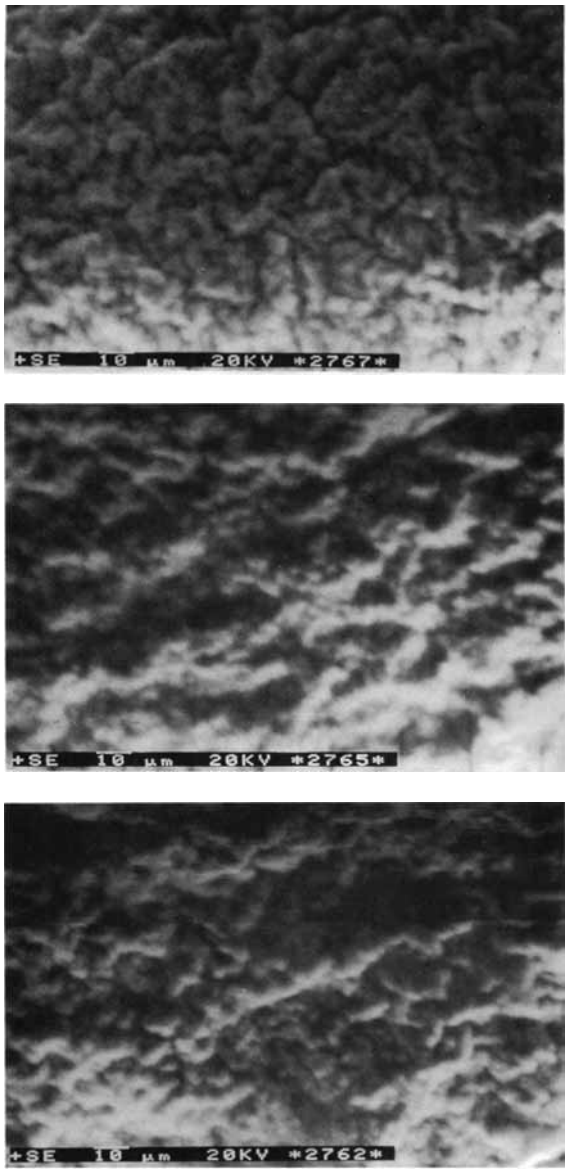

Figure 4 Electron micrographs of TFE–E copolymers obtained at conversions (%): a, 3; b, 9; c, 12.

The microglobules stick into macroglobules at conversions over 6%. The microglobule dimensions were found to increase from 1 to 10 μm with the conversion.

The radical copolymerization of TFE and E was studied in wide range of compositions of the initial monomer mixture (Table I, composition C). The dependence of TFE concentration in the initial monomer mixture on the overall copolymerization rate shows a typical S-shaped curve, and the reaction proceeds in stationary state in the range of TFE content from 60–80 mol % (Fig. 5).

The influence of the total amount of monomers ($\sum$M) on R and molecular weight is shown in Table

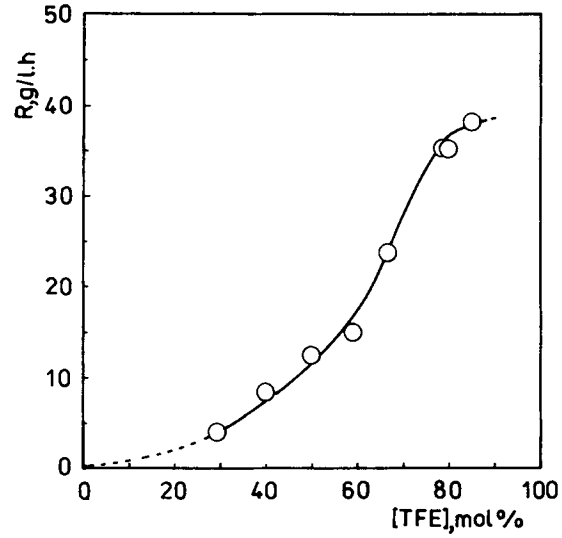

Figure 5 Dependence of copolymerization rate (R) on TFE content in initial monomer mixture. Polymerization conditions as in Table I, composition C.

I, composition D, and the results are presented in Figure 6. This dependence can be described by the equation: $R \propto \sum M^{1.54}$. The high order of the reaction by $\sum$M can be attributed to the participation of monomers in the initiator decomposition reaction, as it has been discussed for other polymerization systems by M. Jodge.[27]

To clarify the dependence of polymer–monomer composition (Table I, composition C), a copolymerization was carried out in batch operation up to conversion of 10% (Fig. 7). Azeotropic copolymerization was observed at TFE content in the initial monomer mixture ca. 34 mol %, which is close to that of the bulk copolymerization (ca. 36 mol %). The content

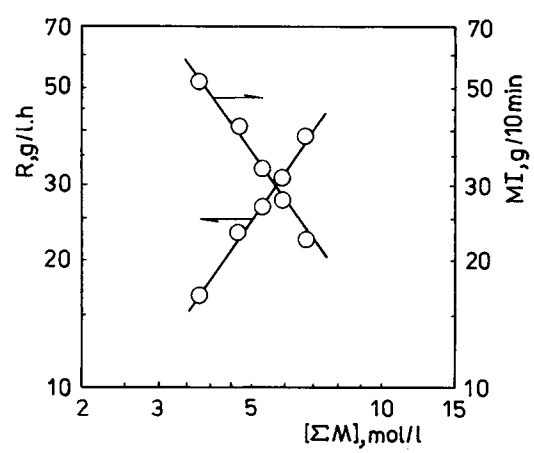

Figure 6 Dependence of copolymerization rate (R) and melt index (MI) on total monomer content ($\sum$M). Polymerization conditions as in Table I, composition D.

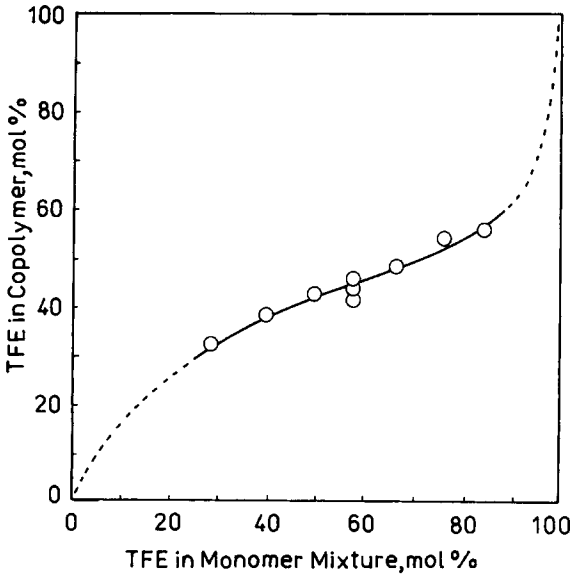

Figure 7 Composition curve of C_2F_4–C_2H_4 copolymerization. Polymerization conditions as in Figure 5.

of C_2F_4 in the copolymer reaches 54 mol % with the increase of TFE content above the azeotropic composition. From the polymer–monomer compositions, using the nonlinear least-squares method,[12] the reactivity ratios of TFE and E were calculated to be r_{TFE} = 0.0646 ± 0.027 and r_E = 0.575 ± 0.09, respectively. The values obtained do not differ much from those of bulk copolymerization.[21] The product of the reactivity ratios (0.037) shows that the copolymer should contain alternating TFE and E units, with the best regularity at TFE content in the initial monomer mixture from 65–80 mol %.

The predominant interaction of the polymer radical with either type of monomer can be attributed to the decrease of the level of the charge transfer complex due to donor–acceptor effect, since there are no steric hindrances in the interaction of TFE with E.

On the bases of the TFE and E reactivity ratios determined and of known Q–e values of E (0.015 and − 0.20 by Young[28] and 0.016 and 0.05 by Greenly[29]), Q–e values of TFE were calculated to be Q_{TFE} = 0.018, e_{TFE} = 1.66; and Q_{TFE} = 0.031, e_{TFE} = 1.87; respectively.

The intramolecular distribution of TFE and E units in the macromolecule calculated in terms of Wall[9] and Gindin et al.[10] (Fig. 8) shows that the most homogeneous composition was obtained at TFE–E molar ratio of 75/25.

The character of the monomer units' distribution in the copolymers synthesized was proved by IR spectroscopy (Fig. 9) and the results are summarized in Table II. The content of sequences $—(C_2H_4)—_2$ (733 cm^{-1} band) and $—(C_2H_4)—_{n\geq 3}$ (721 cm^{-1} band) was lowest for the alternating structures and sharply increased with the disturbance of the monomer units alternation in the copolymer chain.

The distribution of the units in copolymers obtained at TFE–E molar ratio of 75/25 was calculated by the formulae of Gindin et al.[30] (Table III).

The analysis of the obtained results shows that copolymers with highest alternation were obtained at initial molar ratio TFE–E of 75/25, so the next series of experiments was carried out at this ratio.

Furthermore, the copolymerization was carried out in semibatch operation to avoid the conversion inhomogeneity of the copolymers. For this reason, the polymerization system at initial molar ratio TFE–E of 75/25 was fed continuously by a monomer mixture of 50/50 mol % TFE–E, thus keeping constant pressure (± 0.05 MPa).

Figure 10 shows the dependence of R and MI on reaction pressure (Table I, composition E). The increase of the reaction pressure contributes to higher concentration of gaseous monomers in the reaction medium and to increase of R. This is supported also by the enhanced diffusion of TFE and E into the polymer aggregates. The molecular weight increases with pressure (MI decreases).

Further experiments were carried out at 4.2 MPa, which is close to the critical pressure (4.1 MPa) for a TFE–E monomer mixture of 75/25 mol %.

The effect of temperature on copolymer R and MI was studied within the temperature interval of

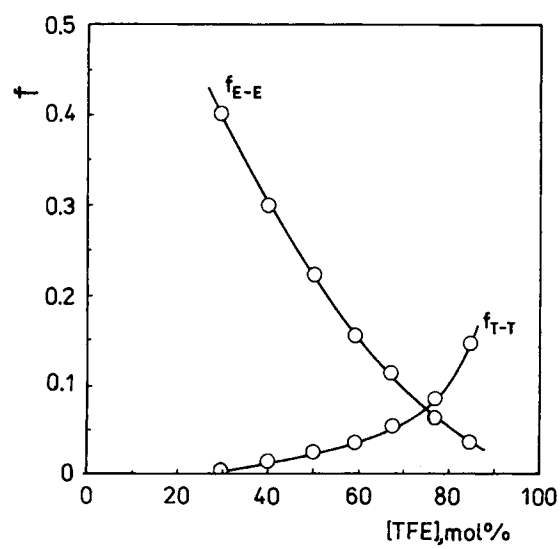

Figure 8 Dependence of probabilities for formation of TFE (f_{T-T}) and E (f_{E-E}) blocks on TFE content in initial monomer mixture.

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

Initial Monomer Mixture TFE–E, mol %	$\frac{\text{Log } I_0/I_{773}\ (n = 1)}{\text{Log } I_0/I_{2973}}$	$\frac{\text{Log } I_0/I_{733}\ (n = 2)}{\text{Log } I_0/I_{2973}}$	$\frac{\text{Log } I_0/I_{721}\ (n \geq 3)}{\text{Log } I_0/I_{2973}}$
85/15	0.20	0.02	0.00
77/23	0.21	0.03	0.02
67/33	0.20	0.10	0.02
59/41	0.21	0.21	0.05
51/49	0.22	0.26	0.05
40/60	0.23	0.48	0.11
30/70	0.17	0.70	0.19

333–344 K (characteristic for AIBN decomposition) (Table I, composition F). The apparent total activation energy (E_a) of TFE–E copolymerization was calculated by Arrhenius equation (Fig. 11) to be 118 kJ/mol. It is lower than that of the bulk copolymerization[21] and is within the range of water-suspension copolymerization of other fluorocontaining monomers.[5] In the temperature interval of 333–344 K, *MI* increases from 8.9 to 49.0 g/10 min with temperature.

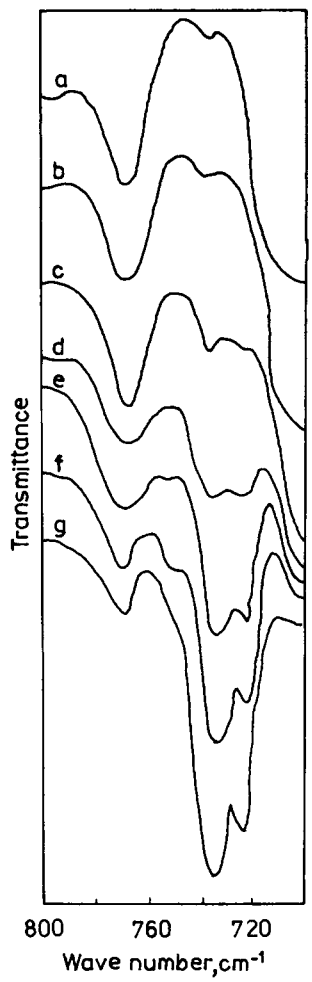

Figure 9 Infrared spectra of TFE–E copolymers in the interval from 700 to 800 cm^{-1} at initial monomer ratio TFE–E (mol %); a, 85/15; b, 77/23; c, 67/33; d, 59/41; e, 51/49; f, 40/60; g, 30/70.

The role of *tert*-BuOH during the reaction of copolymerization is not quite clear yet. AIBN is insoluble in water but dissolves easily in water–alcohol media. It is known that *tert*-BuOH does not affect the decomposition rate of azonitriles, but exerts positive effect on the efficiency of initiation.[31] A series of experiments carried out with composition G from Table I showed that *tert*-BuOH in concentrations over 3.20 mol/L sharply increases *R* (Fig. 12). This proves that alcohol plays the significant role of reaction promoter. Under the same conditions, but without *tert*-BuOH, the reaction rate is rather small. Regardless of the low chain transfer constant ($k = 0.44 \times 10^{-4}$), *tert*-BuOH is the chain transfer agent[32] and, therefore, affects the molecular weight of the copolymers (*MI* increases up to 26 g/10 min). Simultaneously, *tert*-BuOH increases the suspension stability and the copolymer swells in the water–alcohol medium, which facilitates the monomer's diffusion to the active centers.

The increase of TFE–E copolymer thermostability with the *tert*-BuOH content in the polymeriza-

Table III Distribution Functions F_{MI} of monomer sequences in TFE–E copolymer at TFE–E Molar Ratio of 75/25

$-(C_2F_4)-_i$	$F_{(C_2F_4)i}$, mol %	$-(C_2H_4)-_i$	$F_{(C_2H_4)i}$, mol %
(C_2F_4)	35.09	(C_2H_4)	35.13
$(C_2F_4)_2$	11.37	$(C_2H_4)_2$	11.35
$(C_2F_4)_3$	2.76	$(C_2H_4)_3$	2.75
$(C_2F_4)_{>3}$	0.74	$(C_2H_4)_{>3}$	0.81
	49.96		50.04

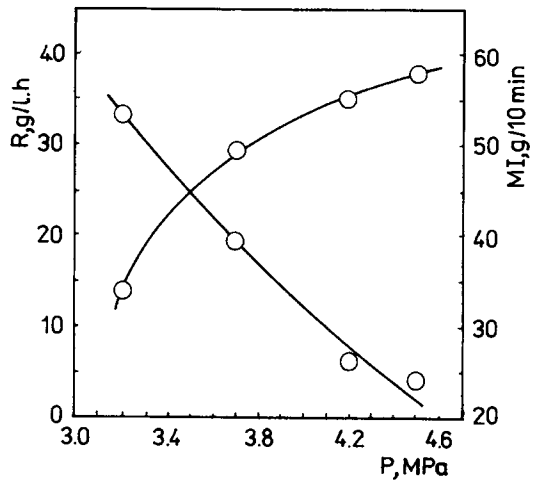

Figure 10 Dependence of copolymerization rate (R) and melt index (MI) on reaction pressure (P). Polymerization conditions as in Table I, composition E.

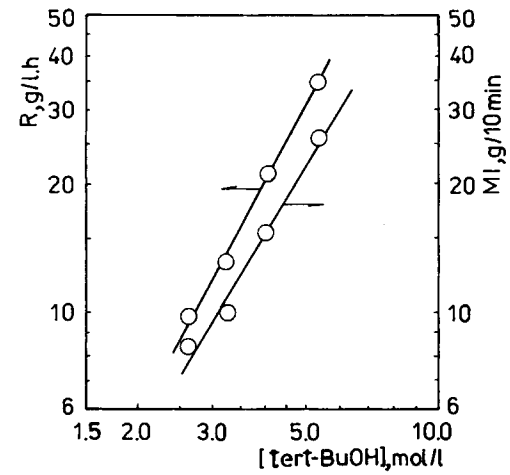

Figure 12 Dependence of copolymerization rate (R) and melt index (MI) on [*tert*-BuOH]. Polymerization conditions as in Table I, composition G.

tion medium was also investigated. The activation energy of thermooxidative decomposition E_d, determined by DTA analyses, increases from 115 to 210 kJ/mol. This can be attributed to the thermostabilizing effect of the end *tert*-butoxy groups which inhibit the dehydrofluorination.[33]

Figure 13 shows the effect of $H_2O/\sum M$ ratio on R and MI at constant pressure. The copolymerization rate and molecular weight decrease with the increase of this ratio. This effect can be explained by the lower monomer concentration in the water phase where initiation and initial growth of radicals takes place. The increase of water phase enhances copolymer swelling and increases segmental mobility of macroradicals and termination rate.

A generalization of the results discussed above provides the possibility of suggesting the following scheme of TFE–E copolymerization:

Initiation

$$In \xrightarrow{k_d} 2R^{\bullet}$$

$$R^{\bullet} + CF_2 = CF_2 \xrightarrow{k_{i1}} R\text{-}CF_2\text{-}\dot{C}F_2$$

$$R^{\bullet} + CH_2 = CH_2 \xrightarrow{k_{i2}} R\text{-}CH_2\text{-}\dot{C}H_2 \qquad (1)$$

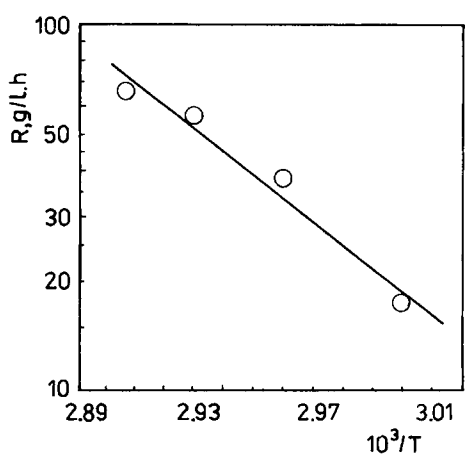

Figure 11 Dependence of copolymerization rate (R) on the temperature (T) in Arrhenius coordinates. Polymerization conditions as in Table I, composition F.

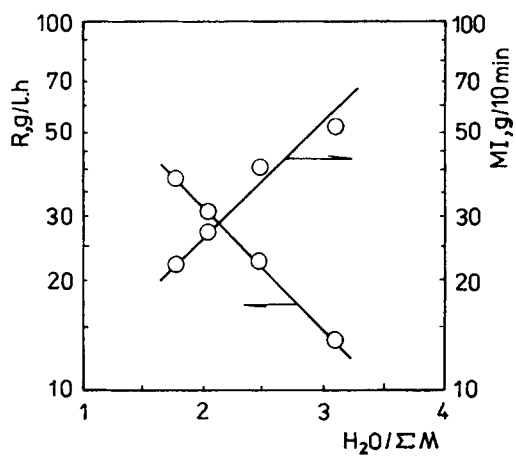

Figure 13 Dependence of copolymerization rate (R) and melt index (MI) on the ratio $H_2O/\sum M$. Polymerization conditions as in Table I, composition D.

Chain growth

$$R\text{-}CF_2\text{-}\dot{C}F_2 + CF_2 = CF_2 \xrightarrow{k_{11}} R\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}\dot{C}F_2 \quad (a)$$

$$R\text{-}CF_2\text{-}\dot{C}F_2 + CH_2 = CH_2 \xrightarrow{k_{12}} R\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}\dot{C}H_2 \quad (b)$$

$$R\text{-}CH_2\text{-}\dot{C}H_2 + CH_2 = CH_2 \xrightarrow{k_{22}} R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\dot{C}H_2 \quad (c)$$

$$R\text{-}CH_2\text{-}\dot{C}H_2 + CF_2 = CF_2 \xrightarrow{k_{21}} R\text{-}CH_2\text{-}CH_2\text{-}CF_2\text{-}\dot{C}F_2 \quad (d) \quad (2)$$

Since reaction (a) proceeds at a high rate (k_{11} = 7400 L/mol s),[34] and taking into account the small value of r_{TFE} (0.0646), then reaction (b) is very fast. The rate of reaction (c) is two orders lower than reaction (a) (k_{22} = 470 L/mol s).[35] Since the value of r_E was found to be 0.576, then reaction (d) is slow, so it limits the alternating copolymerization reaction.

Chain termination:

Chain termination can be accomplished by bimolecular reactions of recombination and disproportionation. Chain termination with participation of AIBN is most unlikely, since AIBN does not participate in the chain transfer reactions. In heterophase reactions, on the other hand, chain transfer to TFE does not take place and chain transfer to E is highly improbable.[4]

Chain transfer is possible only to *tert*-BuOH (regardless of its low transfer constant), thus preserving the kinetic chain.

$$RM_n^{\bullet} + (CH_3)_3COH \rightarrow RM_nH + (CH_3)_3CO^{\bullet} \xrightarrow{initiation} \text{etc.} \quad (3)$$

This was proved by the increased copolymerization rate with *tert*-BuOH concentration in the polymerization system (Fig. 12).

Therefore, the order of the reaction by In (n = 0.9) cannot be attributed to monomolecular chain transfer but takes place due to the heterophase character of the reaction.

The overall copolymerization rate can be described, using the common theory of free-radical copolymerization,[4] as follows:

$$R = \left[\frac{(r_1[M_1] + [M_2])[M_1] + (r_2[M_2] + [M_1])[M_2]}{\dfrac{r_2[M_2]}{k_{22}} + \dfrac{r_1[M_1]}{k_{11}}}\right] \times \sqrt{\frac{R_i}{k_t}} \quad (4)$$

where $[M_1]$ and $[M_2]$ = concentration of TFE and E in initial monomer mixture; R_i = initiation rate; and k_t = termination rate constant.

Differentiation of this expression by $[M_1]$ gives:

$$\frac{dR}{d[M_1]} = \sqrt{\frac{R_i}{k_i}}\left\{\frac{r_2[M_2]}{k_{22}[M_1]}\left[2r_1[M_1]^2 + 2[M_2][M_1]\right] + \frac{r_1}{k_{11}}\left[r_1[M_1]^2 - r_2[M_2]^2\right]\right\} \quad (5)$$

Replacing chain transfer constants and reactivity ratios in (5) at given molar ratios gives:

$$\frac{dR}{d[M_1]} > 0 \quad (6)$$

i.e., the overall copolymerization rate increases with TFE concentration in the monomer mixture. This conclusion confirms the discussion hitherto about the reactions of chain growth and correlates well with the experimental curve in Figure 5.

On the basis of the analysis of the effect of reaction conditions and the components of the polymerization system, a generalized composition (Table I, composition H) was suggested for preparation of copolymers with good complex of properties.

Some of the basic properties of the TFE–E copolymers synthesized are shown in Table IV.

TFE–E copolymers show good mechanical and excellent dielectric properties. Their high resistance to thermoaging (dynamic and static conditions) combines with outstanding inertness to a wide spectrum of chemical agents (acids, bases, organic solvents, sea and distilled water, etc.) (weight gain < 1.0%). The combination of these properties makes this material very interesting for various fields of application; above all, as insulation and engineering materials, working at high temperature and/or in aggressive media.

CONCLUSIONS

The copolymerization of TFE with E in water–alcohol medium initiated by 2,2′-azo-bis-isobutyroni-

Table IV Properties of TFE–E Copolymer

Property	Unit	Value	Test Method
Physical			
Density	kg/m3	1700–1750	Picnometrically
Melt index	g/10 min	26 ± 3	ASTM D-1238-65T
Thermophysical			
Melting point, T_m	K	543	DSC peak
Decomposition temperature, T_d	K	648	DTA peak
$\Delta T = T_d - T_m$	K	105	
Weight loss (at 548 ± 5 K, 5 h)	%	0.3–0.5	
Vicat softening point	K	378	DIN 53460
Mechanical			
Tensile strength	MPa	35.0	ASTM D 638
After dynamic aging	MPa	31.3	
After static aging	MPa	37.3	
Elongation at break	%	310	ASTM D 638
After dynamic aging	%	235	
After static aging	%	285	
Coefficient of friction (dynamic, 0.7 N/mm^2 at 3 m/min)	—	0.5	
Dielectric			
Dielectric constant (1 MHz)	—	2.6	ASTM D 150
Dissipation factor (1 MHz)	—	0.007	ASTM D 150
Dielectric strength	kV/mm	> 33	ASTM D 149
Volume resistivity	Ohm cm	4.1×10^{16}	ASTM D 257

trile proceeds with an induction period and at a higher rate than bulk copolymerization. The dependence of copolymerization rate R and melting index MI on initiator concentration [In] and on total content of monomers [ΣM] was generalized by the following equations:

$$R \propto [\mathrm{In}]^{0.9} [\Sigma \mathrm{M}]^{1.54}$$

$$MI \propto [\mathrm{In}]^{1.44} [\Sigma \mathrm{M}]^{-1.40}$$

Monomer reactivity ratios of TFE–E water-alcohol copolymerization were found to be $r_{TFE} = 0.0646 \pm 0.027$ and $r_E = 0.575 \pm 0.09$, respectively, and the azeotropic point of monomer–polymer composition existed at 34 mol % TFE concentration. High alternating copolymer structure was obtained at TFE–E molar content of 75/25.

A kinetic scheme of the reaction was suggested on the basis of these studies. The attachment of TFE to a macroradical with end E unit was found to be the limiting reaction. The role of the *tert*-BuOH and its accelerating effect on the copolymerization rate was discussed.

The alternating copolymers obtained possess good mechanical, thermal and dielectric properties and show excellent chemical resistance.

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