Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Polymer 45 (2004) 61–70

polymer

www.elsevier.com/locate/polymer

Free radical terpolymerization of three non-homopolymerizable monomers. Part IV. Terpolymerization of maleic anhydride, *trans*-anethole and vinyl-iso-butylether[☆]

Dietrich Braun*, Fengchao Hu

Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, D-64289 Darmstadt, Germany

Received 23 December 2002; received in revised form 17 July 2003; accepted 1 August 2003

Abstract

This paper describes the free radical terpolymerization of maleic anhydride (MSA), *trans*-anethole (ANE) and vinyl-iso-butylether (VIBE) in chloroform, acetonitrile and tetrachloromethane at 60 °C with α,α'-azoisobutyronitrile as initiator. All these monomers are non-homopolymerizable under the used conditions, and the binary copolymerizations take place only between MSA and one of the donor-monomers but not between the two donor-monomers ANE and VIBE. Their reactivity ratios in the binary copolymerizations are all close to zero. The terpolymerizations result in polymers with always about 50 mol% donor- and 50 mol% acceptor monomer units. Against the common MSA-macroradical, VIBE is a little more reactive than ANE in acetonitrile and in chloroform; but in tetrachloromethane ANE is incorporated into the polymers 1.4 times faster than VIBE at the same concentration. The charge transfer complexes between MSA and two donor monomers have only small equilibrium constants and therefore low concentrations in the monomer feeds. But these complexes are more reactive than the free monomers. Their contribution to the total polymerization rate was kinetically determined for the two binary copolymerizations between MSA and one of the two donor monomers in chloroform. At low monomer concentrations the free monomers dominate the overall polymerization rate. At high monomer concentrations the charge transfer complex participates more to the polymerization process.

Keywords: Terpolymerization; Donor monomers; Acceptor monomers

1. Introduction

There are many monomers, which cannot homopolymerize but easily copolymerize. Such monomers usually belong to the groups of electron donors or electron acceptors. During the last years, the radical copolymerization of various functional monomers from these groups as well as the manufacture of new functional polymers with definite structure and special properties has attracted great interest [1,2]. In previous papers [3–5] we have discussed the polymerization mechanisms of binary and ternary systems without participation of homopolymerizable comonomers. In a lot of many publications binary systems of donor- and acceptor-monomers have been studied, but many of the investigated ternary systems are polymerized in the presence of Lewis acids as catalysts or contain at least one homopolymerizable comonomer [6–13]. Up to now only little is known in the field of non-homopolymerizable ternary systems [1,5,14], where the exclusion of the homopolymerizability makes the treatments more simple. All these works have verified that such co- and terpolymerizations lead to co- and terpolymers always with 50 mol% donor and 50 mol% acceptor units in alternating chain sequence.

Maleic anhydride (MSA, $e = 3.7$), *trans*-anethole (ANE, $e = -1.4$) and vinyl-iso-butylether (VIBE, $e = -1.27$) are well-known non-homopolymerizable acceptor- and donor-monomers. Braun et al. [15] have investigated their terpolymerization in tetrahydrofuran and showed the alternating structure of the resulting terpolymers. Alternating co- and terpolymerizations are usually characterized by solvent effects because of the different equilibrium

---

[☆] For parts I, II, and III see Refs. [3–5].

* Corresponding author. Tel.: +49-6151-166866; fax: +49-6151-292855.

E-mail address: dbraun@dki.tu-darmstadt.de (D. Braun).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.08.012

constants for the formation of charge transfer complexes [7]. In the present work the system of MSA, ANE and VIBE is studied in three other solvents (acetonitrile, chloroform and tetrachloromethane).

As all the monomers are non-homopolymerizable and can only copolymerize with another monomer of different electronic type, the alternating polymer chain structure can be easily explained with the terminal model.

Many authors [3,4,16–19] have reported that between donor- and acceptor-monomers charge transfer complexes can be formed and their copolymerization rate has non-linear dependence on the monomer concentration. These results led to the charge transfer complex model and the model of the simultaneous participation of free monomers and charge transfer complexes. With these models the copolymer compositions and the copolymerization kinetics of non-homopolymerizable donor- and acceptor-monomers can be interpreted.

2. Theory

2.1. Terminal model

According to the terminal model [20] the copolymer composition from binary systems is interrelated to the monomer feed by the copolymerization equation (Eq. (1)).

$$\frac{m_1}{m_2} = \frac{[\mathrm{M}_1]}{[\mathrm{M}_2]}\left(\frac{r_1[\mathrm{M}_1]+[\mathrm{M}_2]}{[\mathrm{M}_1]+r_2[\mathrm{M}_2]}\right) \tag{1}$$

Hereby $[\mathrm{M}_i]$ represents the concentration of the monomer M_i in the feed and m_i the amount of the monomer units from M_i in the copolymer, r_i is the reactivity ratio of the monomer M_i in the system.

In a ternary system from one acceptor (M_1) and two donor monomers (M_2, M_3) which are not homopolymerizable and whose binary copolymerizations take place only between one acceptor and one donor but not between two donors, the relationships between the polymer compositions and the monomer feeds according to the terminal-model are given as follows [15] (Eqs. (2)–(4)):

$$\frac{-\dfrac{\mathrm{d}[\mathrm{M}_1]}{\mathrm{d}t}}{-\dfrac{\mathrm{d}[\mathrm{M}_2]}{\mathrm{d}t}} = \frac{m_1}{m_2} = 1 + \frac{k_{13}[\mathrm{M}_3]}{k_{12}[\mathrm{M}_2]} \tag{2}$$

$$\frac{-\dfrac{\mathrm{d}[\mathrm{M}_1]}{\mathrm{d}t}}{-\dfrac{\mathrm{d}[\mathrm{M}_3]}{\mathrm{d}t}} = \frac{m_1}{m_3} = 1 + \frac{k_{12}[\mathrm{M}_2]}{k_{13}[\mathrm{M}_1]} \tag{3}$$

$$\frac{-\dfrac{\mathrm{d}[\mathrm{M}_2]}{\mathrm{d}t}}{-\dfrac{\mathrm{d}[\mathrm{M}_3]}{\mathrm{d}t}} = \frac{m_2}{m_3} = \frac{k_{12}[\mathrm{M}_2]}{k_{13}[\mathrm{M}_3]} \tag{4}$$

Hereby t denotes the reaction time and k_{ij} is the rate constant of the reaction between the macroradical $\sim \mathrm{M}^{\bullet}_i$ and the monomer M_j.

Therefore the reactivity ratio k_{12}/k_{13} corresponds to the reaction of the two donor-monomers M_2 and M_3 versus the acceptor macroradical $\sim \mathrm{M}^{\bullet}_1$. This ratio can be estimated by plotting the terpolymer composition (m_2/m_3) against the feed composition ($[\mathrm{M}_2]/[\mathrm{M}_3]$).

2.2. Penultimate model

The reactivity of propagating chains may be substantially influenced by the nature of penultimate units. For a binary non-homopolymerizable donor–acceptor-system the copolymer is always alternating and composed of equimolecular amounts of donor- and acceptor-units. Therefore, in such binary systems the penultimate model must not be taken into account. The complete assessment of the penultimate effects in a terpolymerization system [21] must be regarded as a formidable task. In the special case where the three monomers cannot homopolymerize and under the prerequisite that a donor-monomer is always followed by an acceptor-monomer the following terpolymerization equation is obtained [15]:

$$\frac{m_2}{m_3} = \frac{k_{312}[\mathrm{M}_2]}{k_{313}[\mathrm{M}_3]}\,\frac{\dfrac{k_{212}[\mathrm{M}_2]}{k_{213}[\mathrm{M}_3]}+1}{\dfrac{k_{312}[\mathrm{M}_2]}{k_{313}[\mathrm{M}_3]}+1} \tag{5}$$

Hereby k_{mnp} is the reaction rate constant between the macroradical $\sim \mathrm{M}_m\mathrm{M}_n^{\bullet}$ and the monomer M_p. During the polymerization the reactivity of a M_1-radical at the chain end is influenced by a monomer unit either from M_2 or M_3 in the penultimate position. Then the ternary system can be described with two relative reactivity ratios R_2^p and R_3^p (Eqs. (6) and (7)):

$$R_2^\mathrm{p} = \frac{k_{212}}{k_{213}} \tag{6}$$

$$R_3^\mathrm{p} = \frac{k_{312}}{k_{313}} \tag{7}$$

The ratio $R_2^\mathrm{p}/R_3^\mathrm{p}$ equals one if the reaction is independent on the penultimate monomer unit.

2.3. Complex model

The cause of a color change at mixing acceptor and donor monomers is the formation of a charge transfer complex. Its concentration can be calculated from the monomer concentrations and the equilibrium constant for the complex formation. According to the complex model [22] a binary copolymerization can be dealt with as a homopolymerization of the complex and the terpolymerization can be described as a binary copolymerization of two complexes.

Binary copolymerization:

$$M_1 + M_2 \overset{K_1}{\rightleftharpoons} C_I$$

$$nC_I \rightarrow \text{poly}(C_I)$$

$$[C_I] = K_1[M_1][M_2] \tag{8}$$

Terpolymerization:

$$M_1 + M_2 \overset{K_1}{\rightleftharpoons} C_I$$

$$M_1 + M_3 \overset{K_2}{\rightleftharpoons} C_{II}$$

$$[C_I] = K_1[M_1][M_2] \tag{9}$$

$$[C_{II}] = K_2[M_1][M_3] \tag{10}$$

$$nC + mC_{II} \rightarrow \text{poly}(C_I\text{-}co\text{-}C_{II})$$

Hereby K_i is the equilibrium constant for the formation of the complexes C_i. According to the charge transfer complex model donor- and acceptor monomer are always in pairs incorporated into polymers and this gives alternating co- and terpolymers as a matter of course. The copolymerization equation for the two 'complex monomers' has the same form as the one for a normal binary copolymerization system (Eq. (11)). Their reactivity ratios r_I and r_{II} can be calculated from the known compositions of the terpolymers and the monomer feeds.

$$\frac{m_2}{m_3} = \frac{d[C_I]}{d[C_{II}]} = \frac{[C_I]}{[C_{II}]}\left(\frac{r_I[C_I] + [C_{II}]}{[C_I] + r_{II}[C_{II}]}\right) \tag{11}$$

As the amounts of the acceptor units in terpolymers always equal 50 mol%, the terpolymerization can be treated as a binary copolymerization of the two donor-monomers (Eq. (12)). Their reactivity ratios R_I and R_{II} can be calculated from r_I and r_{II} with known equilibrium constants K_1 and K_2 (Eqs. (13) and (14)).

$$\frac{m_2}{m_3} = \frac{[M_2]}{[M_3]}\left(\frac{R_I[M_2] + [M_3]}{[M_2] + R_{II}[M_3]}\right) \tag{12}$$

$$R_I = r_I\frac{K_1}{K_2} \tag{13}$$

$$R_{II} = r_{II}\frac{K_2}{K_1} \tag{14}$$

2.4. Simultaneous participation of free monomers and complexes

The free monomer model and the charge transfer complex model can interpret the alternating structure of the resulting co- and terpolymers. But both free monomers and charge transfer complexes exist simultaneously in a system and they can polymerize independently on each other. The above-mentioned models cannot distinguish between their simultaneous participation. Therefore kinetic investigations are needed. According to Braun et al. [3] the overall rate (ν_{br}) of a binary copolymerization between non-homopolymerizable donor and acceptor monomers is the sum of the contributions of the free monomers (ν_f) and the complexes (ν_{CT}) (Eq. (17)).

$$\nu_f = A(X)[M_1] \tag{15}$$

$$\nu_{CT} = A(X)F(X)[M_1]^2 \tag{16}$$

$$\nu_{br} = A(X)[M_1] + A(X)F(X)[M_1]^2 \tag{17}$$

$$\frac{\nu_{br}}{[M_1]} = A(X) + A(X)F(X)[M_1] \tag{18}$$

$$F(X) = K\left(\frac{k_{1C_I}}{k_{12}} + \frac{k_{2C_I}}{k_{21}}X\right) \tag{19}$$

Hereby $A(X)$ and $F(X)$ are constant when the monomer ratio $X = [M_1]/[M_2]$ and the initiator concentration in the monomer feeds for one series of the copolymerizations are the same. The participation of the free monomers changes linearly with the monomer concentration and the contribution of the complexes changes with the monomer concentration in the second order. By study of the dependence of the overall polymerization rate on the monomer concentration at constant X the participation of the free monomers and the complexes can be determined.

3. Experimental part

3.1. Materials

Maleic anhydride (Acros) was purified by sublimation under reduced pressure (0.1 mbar, 50 °C). *Trans*-anethole (Acros) and vinyl-iso-butylether (Fluka) were fractionally distilled over a 20 cm column. α,α′-azoisobutyronitrile was twice recrystallized from absolute ethanol and dried under vacuum over calcium chloride. The solvents chloroform (HPLC, Acros), acetonitrile (99 + %, Acros) and tetrachloromethane (99%, Acros) were used without further purification.

3.2. Determination of the equilibrium constants

The equilibrium constants for the formation of the complexes between donor- and acceptor-monomers were determined in the used solvents (deuterated) at room temperature with the ^{1}H NMR method by Hanna and Ashbaugh [23].

3.3. Polymerization procedure

The polymerizations were carried out in 50 ml Schlenk tubes under N_2-atmosphere at 60 °C with AIBN (10^{-3}–10^{-4} mol/l) as initiator. Before the polymerization they were degassed by three freeze–evacuate–thaw–nitrogen cycles. After 1–3 h polymerization the polymers were obtained by precipitation in a tenfold volume excess of diethyl ether. The precipitated polymers were dried, dissolved in tetrahydrofuran and precipitated in diethyl ether again. The polymers were isolated and dried under reduced pressure at 40 °C to constant weight. In all the polymerizations the conversions were kept below 10 wt%. From the conversion and the polymerization time the overall polymerization rate was calculated.

3.4. Characterization

The co- and terpolymers were characterized by FT-IR (KBr-disc, FTIR-8101M, Shimadzu), ^{1}H NMR (10–20 mg/ml in DMSO-d_6, WM 300, Bruker), MALDI-TOF (4 mg/ml, matrix: dithranol saturated with LiCl, MALDI 4 Shimadzu), GPC (THF as eluent (1 ml/min), 30 °C, PS-standard, RI 410-detector, HPGPC, Waters), TGA (10 °C/min, TGS-2, Perkin–Elmer), DSC (10 °C/min under N_2, 912 DS-DSC, DuPont), etc.

The concentrations of ANE units were determined by UV/VIS-spectroscopy (Specord 200, Analytik Jena) at 277 nm in 1,2-dichloroethane. The MSA units were determined by hydrolysis-titration in THF with 0.1N standard NaOH solution [5]. In case of insolubility of a polymer its composition was determined by elemental microanalysis.

4. Results and discussion

4.1. Synthesis and characterization of the polymers

The binary copolymerizations of MSA/ANE and MSA/VIBE as well as the terpolymerization of MSA/ANE/VIBE took place easily in acetonitrile, chloroform and tetrachloromethane. But during the copolymerization of MSA/ANE and the terpolymerization with high amounts of MSA in the feed polymers were precipitated. All attempts to homopolymerize the single monomers and to copolymerize the two donor-monomers ANE/VIBE under the same conditions as for the terpolymerization failed.

The FT-IR spectrum of the terpolymer shows the characteristic strong double peaks of the stretching vibration of the carbonyl group ($\nu_{C=O}$) of the MSA units at 1780 and 1860 cm^{-1}. The deformation vibration of the C=C bond ($\delta_{C=C}$) in the aromatic ring of the ANE units is seen at 1513 and 1610 cm^{-1} and the deformation vibration of the C–O bond (ν_{C-O}) in VIBE shows the absorption at 1099 cm^{-1}.

In the ^{1}H NMR spectrum of the terpolymer the protons in ANE units have chemical shifts at 1 ppm (β-CH_3), 3.7 ppm (OCH_3) and 7 ppm (aromatic protons). The protons of the alkyl group in VIBE show the chemical shift at 0.5–0.8 ppm. Compared to the both donor-monomers the acceptor-monomer MSA contains just few protons whose chemical shift is shown at 3–4 ppm and is overlapped by other signals.

To be sure that a copolymer is an alternating one, which is composed from donor and acceptor monomer units, the MALDI-TOF spectrum of the binary copolymer poly(MSA-VIBE) was measured (Fig. 1). The mass/charge peaks can be divided into two groups and in each group the peaks are of the same distance of 198 Da next each other, which is exactly the sum of the molar mass of the both monomer units MSA (98.06 Da) and VIBE (100.16 Da). The difference between the two groups is one VIBE-unit. This can be caused by different mechanisms of chain termination. The mass/charge signals in each group are separated in one main peak and many by-peaks. The reason is that both oxygen and carbon have isotopes of different masses, which show statistic dispersities.

According to the GPC-measurements the copolymerizations and the terpolymerization result in only rather low molecular weight polymers (10^3–10^4 g/mol) with a dispersity of $D = 1.4$–2.8. According to the TGA-measurements the copolymer poly(MSA-ANE) has a higher decomposition temperature (350 °C) than poly(MSA-VIBE) (250 °C). The decomposition temperature of the terpolymer is between them (320 °C). The DSC-measurements showed only one glass transition temperature (poly(MSA-VIBE) at 125 °C, poly(MSA-ANE) at 267 °C and for the terpolymer at 145–234 °C). The more ANE units a terpolymer contains, the higher is its glass transition temperature.

All the polymers with ANE units show similar UV/VIS-spectra with absorptions in the range of 200–250 nm and of 260–290 nm. The binary copolymer of MSA/VIBE is US/VIS inactive. The amounts of ANE units in the polymers can be determined from the absorption at 277 nm in 1,2-dichloroethane (A_{277}). The relationship between the ANE concentration and the absorption was calibrated with a copolymer poly(anethole-fumaronitrile) whose composition was determined by microanalysis (Eq. (20)):

$$\mathrm{ANE(g/L)} = 0.10984 \times A_{277} - 0.02098 \tag{20}$$

Hydrolysis of one maleic anhydride unit gives two carboxy groups, which can be titrated with NaOH. If a polymer did not dissolve in 1,2-dichloroethane and tetrahydrofuran, its composition was calculated from the data of the microanalysis.

4.2. Treatment by the terminal- and penultimate model

In Tables 1 and 2 the copolymer compositions depending on the monomer feeds for the binary systems MSA/ANE and MSA/VIBE are shown. Φ_i is the molar fraction of monomer M_i in monomer feed and ϕ_i is the molar fraction of M_i-units in the copolymer. Regardless of the monomer feeds the copolymers are always composed of 50 mol% MSA units and 50 mol% ANE or VIBE units. The graphical

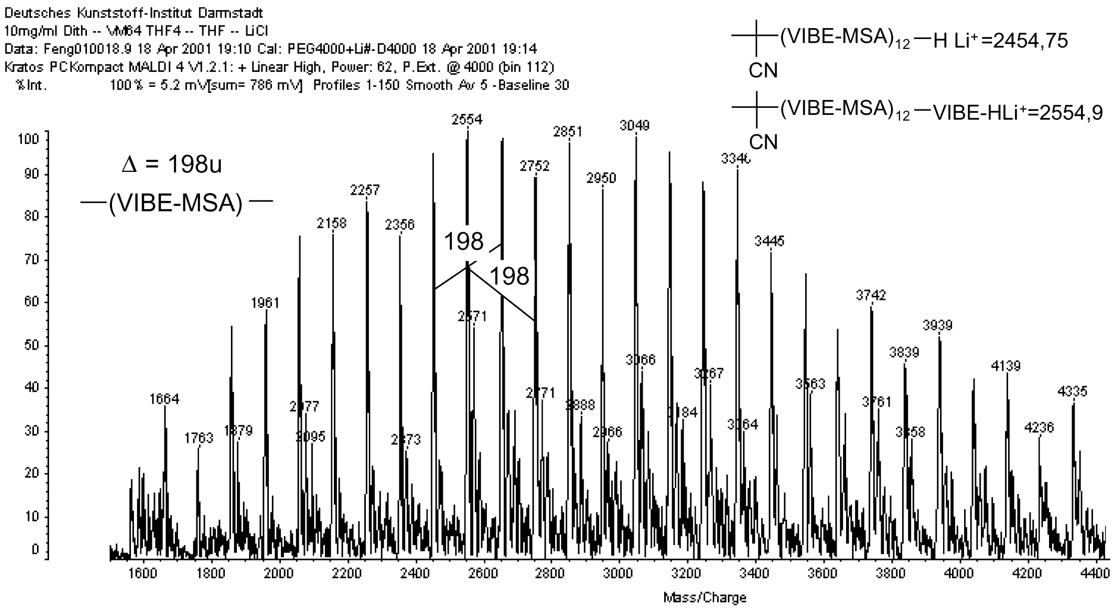

Fig. 1. MALDI-TOF-spectrum of a binary copolymer from the system MSA/VIBE.

regression fitting of the experimental points to the copolymerization equation (Eq. (1)) gives the reactivity ratios of the comonomers r_1 and r_2. Replacement of $[M_i]$ with Φ_i and of m_i with ϕ_i makes no error. They are all close to zero. This indicates an alternating chain growth between these acceptor and donor monomers. To distinguish them from zero the r_1 and r_2 values were rounded to the third decimal place, which of course is not very exact.

The Tables 3–5 give the terpolymer compositions against their monomer feeds. All terpolymers contain about 50 mol% MSA-units and 50 mol% ANE/VIBE-units. Plotting of the compositions of the terpolymers and their monomer feeds gives the Slocombe diagram [24]. In this triangle diagram each arrow describes one terpolymerization system. It starts at the monomer composition and ends at the polymer composition. As an example, in the Slocombe diagram for the system MSA/ANE/VIBE in tetrachloromethane (Fig. 2) all the arrows end close to the line with $\phi_{MSA} = 0.5$, regardless of the monomer feeds. The direction and the length of the arrows show the relative reactivities of the two donor monomers and the difference of the compositions between the terpolymer and its monomer feed. In tetrachloromethane ANE is more reactive than VIBE.

The quantitative treatments of the ternary systems according to the terminal model give the relative reactivities of the two donor-monomers against the common MSA-macroradical. Hereby the ratios of the amounts of the two donor-monomers in terpolymers were given versus the one in the monomer feeds (Tables 3–5 and Fig. 3). Their linear fitting to Eq. (4) gives the slope as the relative reactivity (Table 6). In acetonitrile and chloroform ANE is less reactive than VIBE. As a result the polymers contain a little more VIBE units than the monomer feed. Contrary to that in

Table 1
The copolymerization of $MSA(M_1)/ANE(M_2)$ in chloroform, acetonitrile and tetrachloromethane at 60 °C with AIBN as initiator

Solvent	Φ_1	Φ_2	ϕ_1	ϕ_2	r_1	r_2
Chloroform	0.782	0.218	0.502	0.498	0.001	0.000
	0.574	0.426	0.499	0.501		
	0.375	0.625	0.500	0.500		
	0.183	0.817	0.501	0.499		
Acetonitrile	0.798	0.202	0.498	0.502	0.003	0.001
	0.597	0.403	0.498	0.502		
	0.397	0.603	0.500	0.500		
	0.198	0.802	0.501	0.499		
Tetrachloromethane	0.786	0.214	0.501	0.499	0.001	0.001
	0.602	0.398	0.500	0.500		
	0.402	0.598	0.500	0.500		
	0.201	0.799	0.499	0.501		

Table 2
The copolymerization of $MSA(M_1)/VIBE(M_2)$ in chloroform, acetonitrile and tetrachloromethane at 60 °C with AIBN as initiator

Solvent	Φ_1	Φ_2	ϕ_1	ϕ_2	r_1	r_2
Chloroform	0.772	0.228	0.504	0.496	0.005	0.001
	0.560	0.440	0.502	0.498		
	0.361	0.639	0.502	0.498		
	0.175	0.825	0.499	0.501		
Acetonitrile	0.820	0.180	0.500	0.500	0.000	0.002
	0.630	0.370	0.500	0.500		
	0.431	0.569	0.499	0.501		
	0.221	0.779	0.498	0.502		
Tetrachloromethane	0.830	0.170	0.501	0.499	0.001	0.001
	0.620	0.380	0.500	0.500		
	0.450	0.550	0.499	0.501		
	0.210	0.790	0.499	0.501		

Table 3
The terpolymerization of MSA(M_1)/ANE(M_2)/VIBE(M_3) in chloroform at 60 °C with AIBN as initiator

Φ_1	Φ_2	Φ_3	ϕ_1	ϕ_2	ϕ_3	$\frac{\Phi_2}{\Phi_3}$	$\frac{\phi_2}{\phi_3}$
0.200	0.404	0.396	0.517	0.196	0.287	1.020	0.683
0.400	0.303	0.297	0.507	0.187	0.306	1.020	0.611
0.502	0.101	0.397	0.512	0.093	0.396	0.254	0.235
0.501	0.202	0.297	0.512	0.146	0.342	0.680	0.427
0.500	0.302	0.198	0.481	0.235	0.284	1.525	0.827
0.499	0.402	0.099	0.495	0.322	0.183	4.061	1.760
0.600	0.202	0.198	0.519	0.215	0.266	1.020	0.808
0.800	0.101	0.099	0.531	0.193	0.277	1.020	0.697

tetrachloromethane ANE is 1.4 times faster incorporated into the polymer than VIBE at the same concentration.

In the terpolymer chain from the system MSA/ANE/VIBE, MSA units precede ANE or VIBE units. But before a MSA chain end either an ANE unit or a VIBE unit is possible, which can influence the activity of the macroradical (~ MSA). This effect can be quantitatively estimated with the penultimate model. The graphical fitting (Fig. 3) of Eq. (5) to the experimental points in Tables 3–5 gives the two parameters R_2^p and R_3^p (Table 6). In all three solvents (acetonitrile, chloroform and tetrachloromethane) applies $R_2^p < R_{23}$ and $R_3^p > R_{23}$, which means that ANE as penultimate unit delays the further addition of ANE to the MSA chain end, whereas VIBE as penultimate unit promotes it. It can be seen that the curve for the penultimate model fits better to the experimental points than that for the terminal model.

Neither the terminal model nor the penultimate model can fit absolute satisfactorily the experimental points. Except of measurement errors there is another factor to be taken into account. The length of the polymer chains is at the lower limit to use the 'long chain assumption' for the terminal model and the penultimate model. But effects originating from the primary radical can be neglected, if only the monomer sequence is considered.

4.3. Treatment by the charge transfer complex model

In a mixture of the monomers MSA, ANE and VIBE two 1:1 charge transfer complexes C_I(MSA/ANE) and C_{II}(MSA/VIBE) can be formed. Their concentrations ($[C_I]$, $[C_{II}]$) and molar fractions (Φ_{C_I}, $\Phi_{C_{II}}$) can be calculated from the monomer concentrations and the equilibrium constant (Eqs. (9) and (10)). Therefore the binary copolymerization of MSA/ANE and MSA/VIBE can be dealt with as homopolymerization of C_I or C_{II}; the ternary system MSA/ANE/VIBE changes to a 'binary' system of the complexes C_I and C_{II}, the amounts of the complexes in polymers (ϕ_{C_I}, $\phi_{C_{II}}$) can be calculated from the amounts of the two donor monomer units (Tables 7–9). Their reactivity ratios r_I and r_{II} were determined by the Kelen–Tüdös-method [25] (Table 10). With the calculated reactivity ratios the copolymerization diagrams for the binary system C_I/C_{II} in the used solvents can be plotted (Fig. 4). They describe the experimental results rather well. In acetonitrile the complex C_I shows negligible self-polymerization and the complex C_{II} polymerizes a little more by cross growth with

Table 4
The terpolymerization of MSA(M_1)/ANE(M_2)/VIBE(M_3) in chloroform at 60 °C with AIBN as initiator

Φ_1	Φ_2	Φ_3	ϕ_1	ϕ_2	ϕ_3	$\frac{\Phi_2}{\Phi_3}$	$\frac{\phi_2}{\phi_3}$
0.199	0.406	0.395	0.518	0.232	0.250	1.028	0.928
0.398	0.305	0.296	0.518	0.231	0.251	1.030	0.920
0.501	0.102	0.397	0.521	0.105	0.374	0.257	0.281
0.499	0.204	0.297	0.521	0.198	0.281	0.687	0.705
0.498	0.305	0.197	0.504	0.289	0.207	1.548	1.396
0.496	0.405	0.098	0.497	0.388	0.115	4.133	3.374
0.598	0.204	0.198	0.530	0.270	0.201	1.030	1.343
0.799	0.102	0.099	0.520	0.260	0.221	1.030	1.176

Table 5
The terpolymerization of MSA(M_1)/ANE(M_2)/VIBE(M_3) in tetrachloromethane at 60 °C with AIBN as initiator

Φ_1	Φ_2	Φ_3	ϕ_1	ϕ_2	ϕ_3	$\frac{\Phi_2}{\Phi_3}$	$\frac{\phi_2}{\phi_3}$
0.210	0.400	0.400	0.525	0.312	0.164	1.000	1.902
0.210	0.590	0.200	0.509	0.391	0.100	2.950	3.910
0.400	0.100	0.500	0.541	0.138	0.322	0.200	0.429
0.400	0.200	0.400	0.547	0.236	0.217	0.500	1.088
0.400	0.300	0.300	0.514	0.352	0.134	1.000	2.627
0.420	0.380	0.200	0.544	0.374	0.081	1.900	4.617
0.420	0.480	0.100	0.520	0.407	0.072	4.800	5.653
0.500	0.100	0.400	0.458	0.167	0.375	0.250	0.445
0.500	0.200	0.300	0.563	0.289	0.148	0.667	1.953
0.510	0.290	0.200	0.544	0.353	0.104	1.450	3.394
0.510	0.400	0.100	0.518	0.401	0.082	4.000	4.890
0.600	0.100	0.300	0.517	0.239	0.244	0.333	0.980
0.570	0.230	0.200	0.544	0.351	0.104	1.150	3.375
0.600	0.300	0.100	0.529	0.379	0.092	3.000	4.120

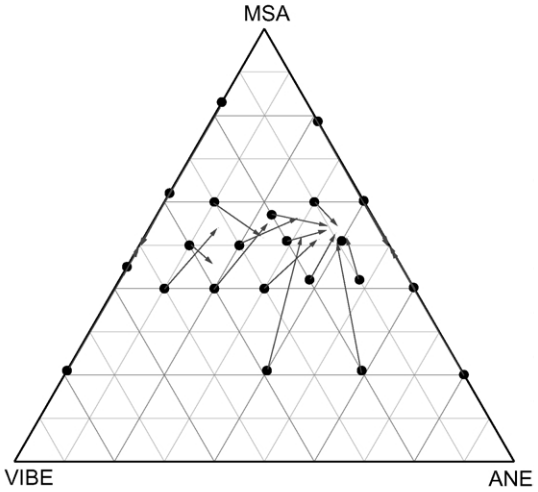

Fig. 2. Slocombe diagram of the system MSA/ANE/VIBE in tetrachloromethane at 60 °C with AIBN as initiator.

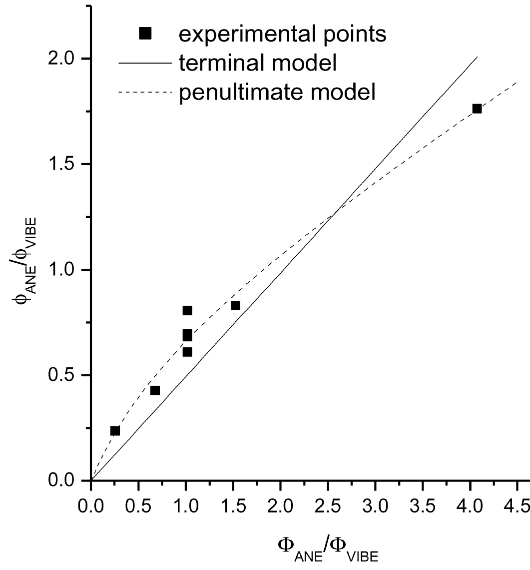

Fig. 3. Terminal and penultimate model for the system MSA/ANE/VIBE in acetonitrile at 60 °C with AIBN as initiator.

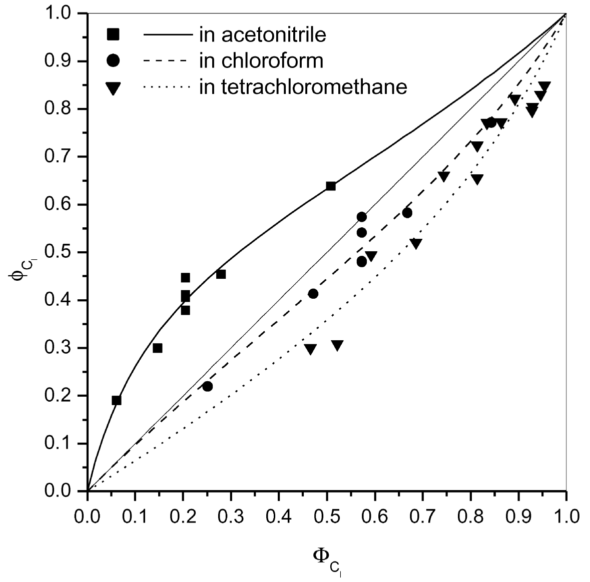

Fig. 4. Copolymerization diagrams of the system C_I(MSA/ANE)/C_{II}(MSA/VIBE) in acetonitrile, chloroform and tetrachloromethane at 60 °C with AIBN as initiator.

Table 6
Relative reactivities and reactivity ratios of ANE to VIBE in the system MSA/ANE/VIBE in acetonitrile, chloroform and tetrachloromethane at 60 °C with AIBN as initiator

Solvent	$R_{23} = \frac{k_{12}}{k_{13}}$	$R_2^p = \frac{k_{212}}{k_{213}}$	$R_3^p = \frac{k_{312}}{k_{313}}$
Acetonitrile	0.492	0.280	1.051
Chloroform	0.871	0.711	1.520
Tetrachloromethane	1.426	1.104	20.635

Table 7
The terpolymerization of MSA/ANE/VIBE in acetonitrile at 60 °C with AIBN as initiator, treatment by the complex model $K_1 = 0.034$, $K_2 = 0.135$

$[C_I]$ (mol/l)	$[C_{II}]$ (mol/l)	Φ_{C_I}	$\Phi_{C_{II}}$	ϕ_{C_I}	$\phi_{C_{II}}$
3.420×10^{-04}	1.327×10^{-03}	0.205	0.795	0.405	0.595
5.130×10^{-04}	1.990×10^{-03}	0.205	0.795	0.379	0.621
2.137×10^{-04}	3.317×10^{-03}	0.061	0.939	0.190	0.810
4.275×10^{-04}	2.488×10^{-03}	0.147	0.853	0.299	0.701
6.412×10^{-04}	1.659×10^{-03}	0.279	0.721	0.454	0.546
8.550×10^{-04}	8.293×10^{-04}	0.508	0.492	0.638	0.362
5.130×10^{-04}	1.990×10^{-03}	0.205	0.795	0.446	0.554
3.420×10^{-04}	1.327×10^{-03}	0.205	0.795	0.411	0.589

C_I. In chloroform both complexes tend a little more to cross polymerization with each other. In tetrachloromethane the complex C_I yields in cross growth with C_{II} and the complex C_{II} rather in homopolymerization.

It is logically to propose that the equilibrium constants for the complex formation at the polymerization temperature (60 °C) are smaller than that at room temperature. But the influence of temperature is the same for both K_1 and K_2, so that the molar fractions of the both complexes have only small dependence on the temperature. Therefore the determined reactivity ratios r_I and r_{II} can be regarded as reliably.

In Tables 3–5 can be seen that the terpolymers contain always about 50 mol% acceptor monomer units (MSA). So the terpolymerization can be similarly dealt with as a binary copolymerization of the two donor monomers ANE and VIBE. Their respective reactivity ratios R_I and R_{II} can be calculated from r_I, r_{II} and the equilibrium constants K_1, K_2. The results are also shown in Table 10. For comparison the copolymerization diagrams of the system MSA/ANE/VIBE in acetonitrile according to the complex model, the penultimate model and the terminal model as example are plotted (Fig. 5). In acetonitrile and in chloroform the penultimate model and the complex model describe the experimental results much better than the terminal model. In tetrachloromethane the complex model describes the measurements at the best.

Comparing the relative reactivities of the two donor monomers and their equilibrium constants with the common

Table 8
The terpolymerization of MSA/ANE/VIBE in chloroform at 60 °C with AIBN as initiator, treatment by the complex model $K_1 = 0.086$, $K_2 = 0.066$

$[C_I]$ (mol/l)	$[C_{II}]$ (mol/l)	Φ_{C_I}	$\Phi_{C_{II}}$	ϕ_{C_I}	$\phi_{C_{II}}$
8.881×10^{-04}	6.622×10^{-04}	0.573	0.427	0.481	0.519
1.332×10^{-03}	9.933×10^{-04}	0.573	0.427	0.480	0.520
5.551×10^{-04}	1.656×10^{-03}	0.251	0.749	0.219	0.781
1.110×10^{-03}	1.242×10^{-03}	0.472	0.528	0.413	0.587
1.665×10^{-03}	8.278×10^{-04}	0.668	0.332	0.582	0.418
2.220×10^{-03}	4.139×10^{-04}	0.843	0.157	0.771	0.229
1.332×10^{-03}	9.933×10^{-04}	0.573	0.427	0.574	0.426
8.881×10^{-04}	6.622×10^{-04}	0.573	0.427	0.541	0.459

Table 9
The terpolymerization of MSA/ANE/VIBE in tetrachloromethane at 60 °C with AIBN as initiator, treatment by the complex model $K_1 = 0.480$, $K_2 = 0.110$

$[C_I]$ (mol/l)	$[C_{II}]$ (mol/l)	Φ_{C_I}	$\Phi_{C_{II}}$	ϕ_{C_I}	$\phi_{C_{II}}$
0.081	0.018	0.814	0.186	0.655	0.345
0.119	0.009	0.928	0.072	0.796	0.204
0.038	0.044	0.466	0.534	0.300	0.700
0.077	0.035	0.686	0.314	0.521	0.479
0.115	0.026	0.814	0.186	0.724	0.276
0.153	0.018	0.892	0.108	0.822	0.178
0.194	0.009	0.954	0.046	0.850	0.150
0.048	0.044	0.522	0.478	0.308	0.692
0.096	0.033	0.744	0.256	0.661	0.339
0.142	0.022	0.864	0.136	0.772	0.228
0.196	0.011	0.946	0.054	0.830	0.170
0.058	0.040	0.593	0.407	0.495	0.505
0.126	0.025	0.834	0.166	0.771	0.229
0.173	0.013	0.929	0.071	0.805	0.195

acceptor monomer (MSA) (Tables 6 and 10) shows that in this system there is no certain interrelation between the reactivities of the complexes or the donor monomers and the equilibrium constants for the formation of their complexes, because the equilibrium constants can only influence the complex concentration, but not its reactivity which is depended on its structure.

4.4. Treatment by the model of simultaneous participation of free monomers and complexes

In a polymerization system of electron donors and electron acceptors free monomers and charge transfer complexes exist side by side. They take part in the polymerization simultaneously. For the quantitative estimation of their participation the overall polymerization rates were measured for the systems MSA/ANE and MSA/VIBE in chloroform with constant monomer ratios $X = [M_1]/[M_2]$ and different monomer concentrations (Tables 11 and 12).

Table 10
Reactivity ratios according to the complex model for the system MSA/ANE/VIBE(C_I/C_{II}) in acetonitrile, chloroform and tetrachloromethane at 60 °C with AIBN as initiator

Solvent	K_1	K_2	r_I	r_{II}	R_I	R_{II}
Acetonitrile	0.034	0.135	1.049	0.231	0.265	0.913
Chloroform	0.086	0.066	0.558	0.941	0.727	0.722
Tetrachloromethane	0.480	0.110	0.446	1.589	1.946	0.364

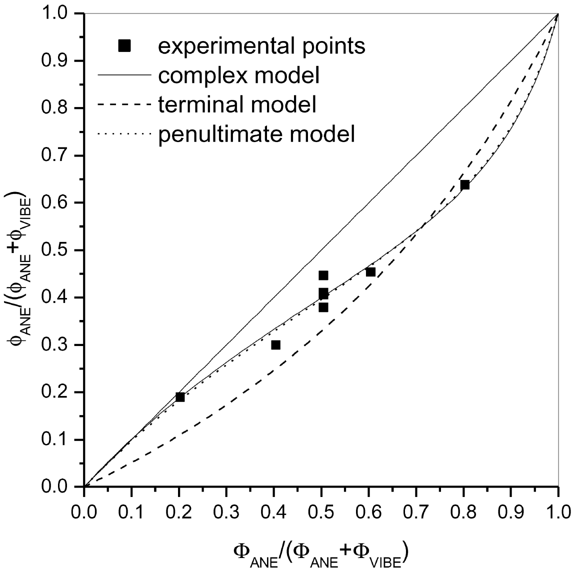

Fig. 5. 'Copolymerization' diagram of the two donor monomers in the system (MSA)/ANE/VIBE in acetonitrile at 60 °C with AIBN as initiator.

Plotting of the quotient v_{br}/[ANE] against [ANE] in the system MSA/ANE for different monomer ratios [MSA]/[ANE] shows nearly straight lines (Fig. 6). The linear fitting of the kinetic equation (Eq. (18)) to these points gives the rate coefficients $A(X)$ and $F(X)$. With those the participations of the free monomers and the charge transfer complexes to the overall polymerization rate can be calculated (Eqs. (15) and (16)). As an example the partial rates and their sum for the binary system at the monomer ratio $X = [MSA]/[ANE] = 0.6498$ have been drawn in the same diagram (Fig. 7). The sum curve describes the experiments very well. It also shows that at lower monomer concentrations the free monomers dominate the overall polymerization rate. But the participation of the charge transfer complexes increases much faster with the monomer concentration and exceeds quickly over the part of the free monomers at a 'critical' point $[ANE]_c$. For example, at [ANE] = 0.1 mol/l, the overall polymerization rate is composed to 80% by the part of free monomers and only to 20% by the part of the complex. Above $[ANE]_c$ at [ANE] = 0.8 mol/l, the overall polymerization rate is

Table 11
Kinetic measurements of the system MSA/ANE ($K = 0.086$) in chloroform at 60 °C and varying $X = \frac{[MSA]}{[ANE]}$ with AIBN as initiator $[AIBN] = 2.35 \times 10^{-3}$ mol/l

X	[ANE] (mol/l)	v_{br} (mol/l·s)	$F(X)$	$A(X)$	$[ANE]_c$ (mol/l)
0.2437	1.2775	8.64×10^{-06}	2.5	1.71×10^{-6}	0.40
	0.7984	4.75×10^{-06}			
	0.3194	8.37×10^{-07}			
	0.1597	3.87×10^{-07}			
0.6498	0.7186	1.22×10^{-05}	2.5	6.00×10^{-6}	0.40
	0.4790	7.66×10^{-06}			
	0.2395	2.25×10^{-06}			
1.4621	0.6387	2.40×10^{-05}	0.8	2.50×10^{-5}	1.25
	0.4790	1.70×10^{-05}			
	0.3194	1.05×10^{-05}			
	0.1597	4.41×10^{-06}			
3.8988	0.3194	2.86×10^{-05}	3.0	5.00×10^{-5}	0.33
	0.1996	1.74×10^{-05}			
	0.0798	4.75×10^{-06}			
	0.0399	1.93×10^{-06}			

Table 12
Kinetic measurements of the system MSA/VIBE ($K = 0.066$) in chloroform at 60 °C with AIBN as initiator $[\text{AIBN}] = 1.30 \times 10^{-3}$mol/l ($X = 1.004$)

[VIBE] (mol/l)	v_{br} (mol/l·s)	$F(X)$	$A(X)$	$[\text{VIBE}]_c$ (mol/l)
0.6580	1.26×10^{-04}	0.4	1.5×10^{-4}	2.5
0.3948	6.78×10^{-05}			
0.2632	4.35×10^{-05}			
0.1316	2.13×10^{-05}			
0.1645	2.73×10^{-05}			

determined to 33% by free monomers and 67% by the complex.

According to the complex model the highest polymerization rate is obtained at the equimolar monomer feed of MSA and ANE. But Fig. 8 shows the highest rate at the ANE molar fraction of $\Phi_{\text{ANE}} = 0.6$. This also verifies that free monomers as well as charge transfer complexes participate to the polymerization process. The two donor monomers have different reactivities versus the common acceptor macroradical. And their cumulative polymerization rate increases with the molar fraction of the more reactive donor monomer (here ANE). The maximum overall polymerization rate from free monomers and the charge transfer complexes is shown at $X > 0.5$.

Because of the small equilibrium constant the concentration of the complex is much smaller than the monomer concentrations in the monomer feed, but it participates noticeable or even dominant in the polymerization process. This means that the complex is of much higher reactivity than the free monomers.

According to Eq. (19), plotting of F(X) against X results nearly in a straight line with an intercept of 1.94 and a slope of 0.4. With the known $K = 0.086$ the relative reactivities between the charge transfer complex and the free monomers can be calculated to $\frac{k_{1C_I}}{k_{12}} = 22.6$ and $\frac{k_{2C_I}}{k_{21}} = 4.7$. Therefore, against the macroradical ~ MSA· the complex C_I is 23 times more reactive than the free ANE; against the macroradical ~ ANE· the complex is about 5 times more reactive than the free MSA.

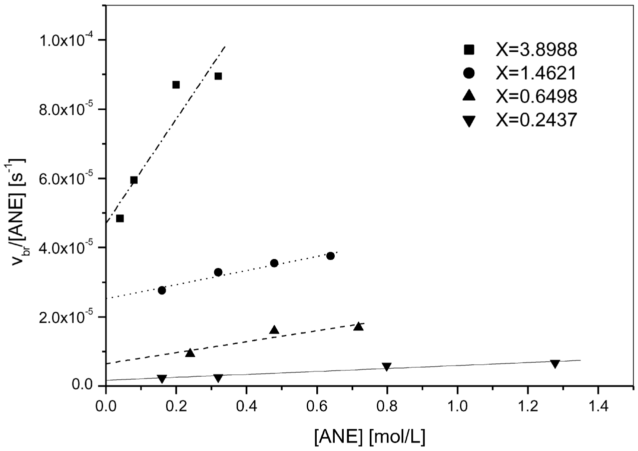

Fig. 6. Plot of the quotient $v_{br}/[\text{ANE}]$ against [ANE] for the system MSA/ANE in chloroform at varying $X = [\text{MSA}]/[\text{ANE}]$ with 2.35×10^{-3} mol/l AIBN at 60 °C.

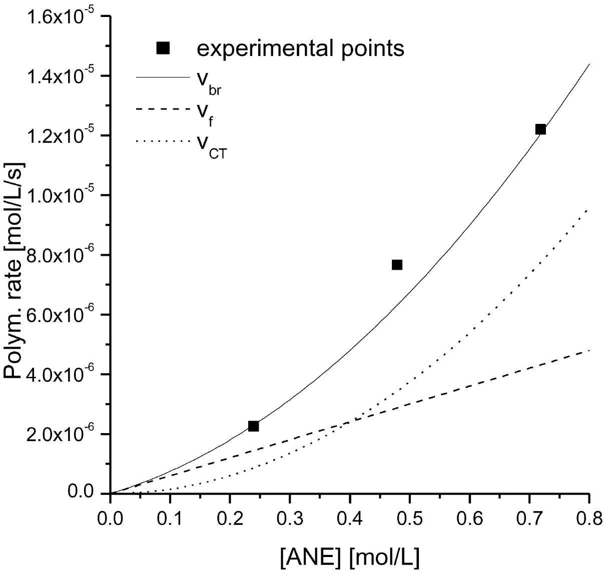

Fig. 7. Kinetic measurement of the binary system MSA/ANE ($X = 0.6498$) in chloroform at 60 °C with AIBN as initiator, $[\text{AIBN}] = 2.35 \times 10^{-3}$mol/l.

As mentioned the equilibrium constants were determined at a lower temperature (~23 °C) than the polymerization temperature (60 °C). The higher the temperature is, the smaller is the equilibrium constant and so the complex concentration. Therefore the real reactivities of the charge transfer complexes are even higher than that we have determined.

The kinetics of the system MSA/VIBE in chloroform (Table 12) was measured only at one monomer ratio and can be similarly treated as the system MSA/ANE. The results are shown in Figs. 9 and 10. In this system in a wide range of monomer concentration the free monomers influence more strongly the whole polymerization process. For example at

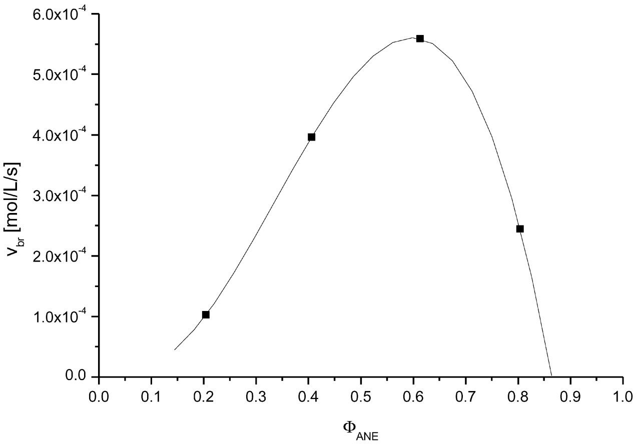

Fig. 8. Plot of v_{br} against the mol fraction of ANE in the system MSA/ANE in chloroform with $[\text{AIBN}] = 2.35 \times 10^{-3}$ mol/l at 60 °C $[\text{M}] = 1.20$ mol/l.

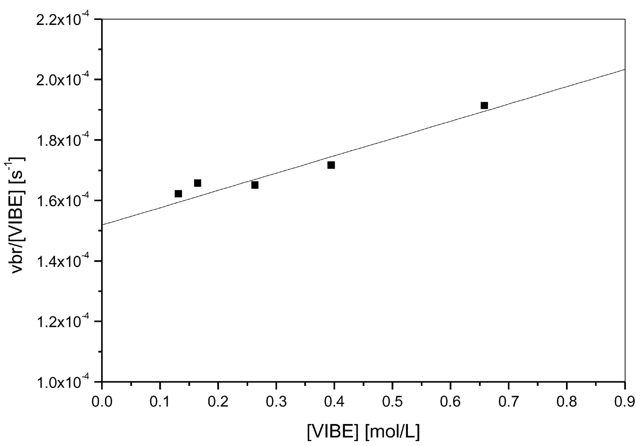

Fig. 9. Plot of the quotient v_{br}/[VIBE] against [VIBE] for the system MSA/VIBE ($X = 1.0040$) in chloroform with 1.30×10^{-3} mol/l AIBN at 60 °C.

[VIBE] = 0.7 mol/l, the total polymerization rate is determined to 71% by free monomers and only to 29% by the charge transfer complex.

5. Conclusions

MSA, ANE and VIBE cannot homopolymerize but MSA and ANE as well as MSA and VIBE can easily copolymerize. At these binary copolymerizations and the terpolymerization of MSA/ANE/VIBE polymers with always 50 mol% MSA units and 50 mol% ANE/VIBE units are obtained. In the binary copolymerizations all the monomers have reactivity ratios close to zero. The alternating structure of the polymers can be explained by the terminal model, the penultimate model and the charge transfer complex model.

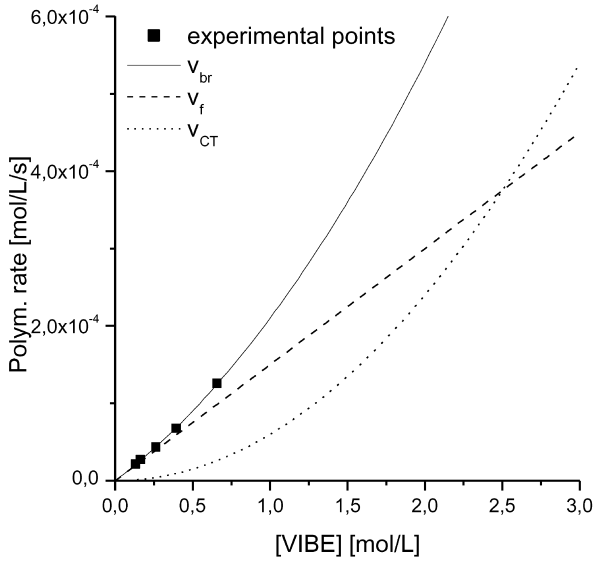

Fig. 10. Kinetic measurement of the binary system MSA/VIBE ($X = 1.0040$) in chloroform at 60 °C with AIBN as initiator, [AIBN] = 1.30×10^{-3} mol/L.

Against the common MSA-macroradical ANE is a little less reactive than VIBE in acetonitrile and chloroform. This is similar as in tetrahydrofuran. In tetrachloromethane ANE is a little more reactive than VIBE. In acetonitrile and chloroform ANE or VIBE show only small penultimate effects on the reactivity of MSA-macroradical, in tetrachloromethane it is somewhat stronger.

The binary copolymerization proceeds simultaneously by free monomers and preformed charge transfer complexes. The complexes have only small equilibrium constants and low concentrations in the monomer feed. But they are much more reactive than the free monomers and contribute to the total polymerization process. The kinetic measurements of a ternary system (VIBE/MSA/fumaronitrile (in preparation)) and the studied binary systems lead to the same results: At low monomer concentrations the free monomers dominate the overall polymerization rate. At higher monomer concentrations the charge transfer complexes determine the polymerization process.

Acknowledgements

Financial support from Max-Buchner–Forschungsstiftung is gratefully acknowledged.

References

[1] Rzaev ZMO. Prog Polym Sci 2000;24:163–217.
[2] Drent E, Budzelaar M. Chem Rev 1996;96:663–81.
[3] Braun D, Elsässer H. Macromol Theory Simul 2000;9:177–80.
[4] Braun D, Elsässer H. Macromol Chem Phys 2000;201:2103–7.
[5] Braun D, Elsässer H, Hu F. Eur Polym J 2001;37:1779–84.
[6] Brown PG, Fujimori K. Polymer 1995;35:1053–9.
[7] Giese B. Angew Chem 1983;95:771–82.
[8] Hall HK, Padias AB. J Polym Sci, Part A: Polym Chem 2001;39: 2067–9.
[9] Kuran W, Pasynkiewicz S, Nadir R. Makromol Chem 1977;178: 1873–9.
[10] Furukawa J, Kobayashi E, Wakui T. Polym Preprint 1979;20:547–50.
[11] Florjanczyk Z, Krawiec W. Makromol Chem 1988;189:53–65.
[12] Iwatsuki S, Shin M, Yamashita Y. Makromol Chem 1967;102: 232–44.
[13] Iwatsuki S, Itho T, Sato T. Macromolecules 1986;19:1800–3.
[14] Iwatsuki S, Yamashita Y. Makromol Chem 1967;104:263–74.
[15] Braun D, Schacht M, Elsässer H, Tüdös F. Macromol Rapid Commun 1997;18:335–42.
[16] Furukawa J, Kobayashi E. Rubb Chem Tech 1978;51:600–46.
[17] Iwatsuki S, Yamashita Y. Prog Polym Sci (Japan) 1971;2:1–48.
[18] Iwatsuki S, Yamashita Y. Makromol Chem 1965;89:205–13.
[19] Iwatsuki S, Itho T, Hiraiwa A. Makromol Chem 1981;182:2161–74.
[20] Mayo FR, Lewis FM. J Am Chem Soc 1944;66:1594–601.
[21] Ham GE. J Polym Sci Part A: Polym Chem 1964;2:4191–200.
[22] Bartlett PD, Nozaki K. J Am Chem Soc 1946;68:1495–504.
[23] Hanna MW, Ashbaugh AL. J Polym Chem 1964;68:811–6.
[24] Slocombe RJ. J Polym Sci 1957;26:9–22.
[25] Kelen T, Tüdös F. J Macromol Sci Chem 1975;A9:1–27.