Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Braun, Dietrich and Hu, Fengchao(2005) 'Free Radical Terpolymerization of Trans-Anethole, Maleic Anhydride and N-Ethylmaleimide', Journal of Macromolecular Science, Part A, 42: 9, 1127 — 1146

To link to this Article: DOI: 10.1080/10601320500189299

URL: http://dx.doi.org/10.1080/10601320500189299

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 42:1127–1146, 2005
Copyright © Taylor & Francis, Inc.
ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320500189299

Free Radical Terpolymerization of Trans-Anethole, Maleic Anhydride and N-Ethylmaleimide

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Trans-anethole (ANE) and maleic anhydride (MSA) do not homopolymerize in tetrahydrofuran and in chloroform with α,α'*-azoisobutyronitrile (AIBN) as initiator. In comparison, N-ethylmaleimide (NEMI) is homopolymerized very slowly. From these monomers, three binary systems have been studied and their copolymerization ratios were determined at 60°C: ANE/MSA* ($r_1 = 0.002$, $r_2 = 0.001$ *(in THF)), ANE/NEMI* ($r_1 = 0.033$, $r_2 = 0.284$ *(in THF) and* $r_1 = 0.079$, $r_2 = 0.097$*(in* $CHCl_3$*)) and MSA/NEMI* ($r_1 = 0.158$, $r_2 = 1.676$ *(in THF) and* $r_1 = 0.070$, $r_2 = 2.677$ *(in* $CHCl_3$*)). The terpolymerization of these three monomers results in polymers with more than 50 mol% acceptor-monomer (MSA, NEMI) units. The equilibrium constants for the formation of charge-transfer complexes between the donor(ANE) and the acceptors(MSA or NEMI) were determined with the* ^{1}*H-NMR method* K_I*(ANE/MSA) = 0.12 and 0.09, respectively.* K_{II}*(ANE/NEMI) = 0.07 and 0.04 in THF and* $CHCl_3$*). According to the model of the simultaneous participation of free monomers and complexes, the equations for the overall polymerization rate of co- and terpolymerization, with participation of one homopolymerizable monomer, were derived at the first time. The participation of free monomers and complexes to the polymerization process were determined via kinetic measurements. At low monomer concentrations, free monomers dominate, and at high monomer concentrations, the more active complexes determine the overall polymerization rate. The maximum polymerization rate was not always at the 1 : 1-monomer composition and changes with the monomer concentration. The solvent effect on the polymer compositions and on the polymerization kinetics was discussed.*

Keywords terpolymerization, CT-complex, kinetic

Introduction

Maleic anhydride (MSA) and trans-anethole (ANE) are well-known non-homopolymerizable acceptor- respective donor-monomers, but they can easily copolymerize with each other (1). Information about the homopolymerizability of the N-substituted maleimide is controversial. According to Braun (2) N-ethylmaleimide (NEMI) is similar to MSA non-homopolymerizable under usual free radical conditions, but Wang et al. and

Received and Accepted February 2005

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Raetzsch (3, 4) have reported on the successful polymerization of N-alkylmaleimide in different solvents.

The free radical copolymerization of acceptor and donor monomers usually results in alternating copolymers. For an explanation of this process, two mechanisms have been applied: the free monomer model (5–7) and the charge-transfer complex model (8). The free monomer model is based on cross reactions between the donor and the acceptor monomers. According to this model, the donor monomer can only add to an acceptor macroradical and vice versa. The charge-transfer complex (CTC) model proposes the formation of 1 : 1 binary complexes between the donor and the acceptor monomers before their polymerization, which then can homopolymerize (in the case of binary copolymerizations) or copolymerize (in the case of terpolymerizations). Both the free monomer model and the CT-complex model can satisfactorily explain the cases in which polymer compositions with 50 mol% acceptor- and 50 mol% donor monomer units were obtained. However, in reality, free monomers and CT-complexes take part in the polymerization process simultaneously. Neither of the mentioned models can distinguish their participation only from the overall polymer compositions.

CT-complexes are usually much more reactive than free monomers. Therefore, the participation of free monomers and complexes in the copolymerization process results in different dependency on the monomer concentrations and on the monomer compositions. The calculations of Braun et al. (9) have made it possible to estimate the contributions of free monomers and CT-complexes in alternating binary copolymerizations and in terpolymerizations of non-homopolymerizable donor- and acceptor-monomers. The kinetics of terpolymerization with participation of one homopolymerizable monomer is more complex and till now is not studied in the literature. In this work, we amplify the model by Braun for this case. Recently, Liu et al.(10) have extended the kinetic model for binary systems concerning the participation of CT-complexes and the homopolymerization of free monomers and included kinetic- or diffusion-controlled termination into one equation.

Theory

As a result of different polarity, charge-transfer complexes can be formed between acceptor- and donor monomers. In such a system of acceptors and donors, free monomers and the formed CT-complexes are always in equilibrium. When M_1 is a donor monomer and M_2, and M_3 are acceptor monomers, the following reactions are possible:

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

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

Free monomers M_1, M_2, and M_3 as well as the CT-complexes C_I and C_{II} can take part in the polymerization process simultaneously. According to Braun et al. (9) the total polymerization rate of a binary copolymerization or a terpolymerization of non-homopolymerizable donor-/acceptor-monomers is the sum of two partial polymerization rates of free monomers and charge-transfer complexes, when the initiator concentration and the acceptor/donor-monomer ratios in the feeds are kept constant.

Binary Copolymerization of Two Non-Homopolymerizable Acceptor- and Donor Monomers (Equations 1–5)

$$v_{br} = A(X)[M_1] + A(X)F(X)[M_1]^2 \tag{1}$$

$$v_f = A(X)[M_1] \tag{2}$$

$$v_{CT} = A(X)F(X)[M_1]^2 \tag{3}$$

with

$$A(X) = \frac{2k_{12}v_i^{0.5}X}{(k_{t11} + 2k_{t12}(k_{12}/k_{21})X + k_{t22}((k_{12}/k_{21})X)^2)^{0.5}} \tag{4}$$

$$F(X) = K_1\left(\frac{k_{1C_I}}{k_{12}} + \frac{k_{2C_I}}{k_{21}}X\right) \tag{5}$$

(M_i)	*concentration of M_i in monomer feed*
v_{br}	*overall polymerization rate*
v_f	*partial polymerization rate of free monomers*
v_{CT}	*partial polymerization rate of charge-transfer complexes*
X	*monomer ratio $(M_2)/(M_1)$ in monomer feed*
$A(X)$, $F(X)$	*constant coefficients*
k_{ij}	*reaction constant of propagation*
k_{tij}	*reaction constant of termination*
v_i	*start rate of the polymerization*
K_i	*equilibrium constant for the formation of charge-transfer complex*

Terpolymerization of One Donor- and Two Acceptor Monomers, which are all Non-Homopolymerizable (Equations 6–8)

$$v_{br} = A(X_1, X_2)[M_1] + A(X_1, X_2)F(X_1, X_2)[M_1]^2 \tag{6}$$

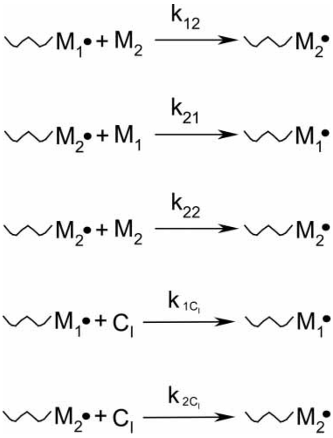
$$v_f = A(X_1, X_2)[M_1] \tag{7}$$

$$v_{CT} = A(X_1, X_2)F(X_1, X_2)[M_1]^2 \tag{8}$$

Keeping X_1, X_2 and initiator concentration constant, $A(X_1,X_2)$ and $F(X_1,X_2)$ are also constant.

Binary Copolymerization of One Homopolymerizable and One Non-Homopolymerizable Acceptor- and Donor Monomers

The kinetics of the copolymerization with one homopolymerizable monomer in addition to non-homopolymerizable monomers is different only in the chain propagation steps, the chain initiation and termination reactions are the same. Instead of four chain propagation steps in the case of binary copolymerization with non-homopolymerizability of both monomers, there are five propagation possibilities in the binary copolymerization of one non-homopolymerizable and one homopolymerizable monomer. When M_1 is non-homopolymerizable, and M_2 is homopolymerizable, and C_I is the formed charge-transfer complex from M_1 and M_2, the following five chain propagation steps are possible:



On the assumption of a steady state, the building rate of the radicals $\sim M_2\cdot$ is equal to its disappearance:

$$k_{12}[\sim M_1\cdot][M_2] = k_{21}[\sim M_2\cdot][M_1] \tag{9}$$

$$[\sim M_2\cdot] = \frac{k_{12}[M_2]}{k_{21}[M_1]}[\sim M_1\cdot] \tag{10}$$

The chain initiation rate v_i is equal the termination rate v_t:

$$v_i = v_t = k_{t11}[\sim M_1\cdot]^2 + 2k_{t12}[\sim M_1\cdot][\sim M_2\cdot] + k_{t22}[\sim M_2\cdot]^2 \tag{11}$$

From Equations 10 and 11, the radical concentration $[\sim M_1\cdot]$ can be calculated:

$$[\sim M_1\cdot] = \frac{v_i^{0.5}}{(k_{t11} + 2k_{t12}([M_2]/[M_1])(k_{12}/k_{21}) + k_{t22}((k_{12}/k_{21})[M_2]/[M_1])^2)^{0.5}} \tag{12}$$

The total polymerization rate is:

$$\begin{aligned} v_{br} &= -\frac{d([M_1]+[M_2])}{dt} \\ &= k_{12}[\sim M_1\cdot][M_2] + k_{21}[\sim M_2\cdot][M_1] + k_{22}[\sim M_2\cdot][M_2] \\ &\quad + 2(k_{1C_l}[\sim M_1\cdot][M_2M_1] + k_{2C_l}[\sim M_2\cdot][M_1M_2]) \end{aligned} \tag{13}$$

V_{br} can be divided into two partial polymerization rates of free monomers v_f and complexes v_{CT}:

$$v_f = k_{12}[\sim M_1\cdot][M_2] + k_{21}[\sim M_2\cdot][M_1] + k_{22}[\sim M_2\cdot][M_2] \tag{14}$$

$$v_{CT} = 2(k_{1C_l}[\sim M_1\cdot][M_2M_1] + k_{2C_l}[\sim M_2\cdot][M_1M_2]) \tag{15}$$

Insertion of Equations 10 and 12 in Equations 14 and 15 gives:

$$v_{br} = A'(X)[M_1] + A'(X)F'(X)[M_1]^2 \tag{16}$$

$$v_f = A'(X)[M_1] \tag{17}$$

$$v_{CT} = A'(X)F'(X)[M_1]^2 \tag{18}$$

with:

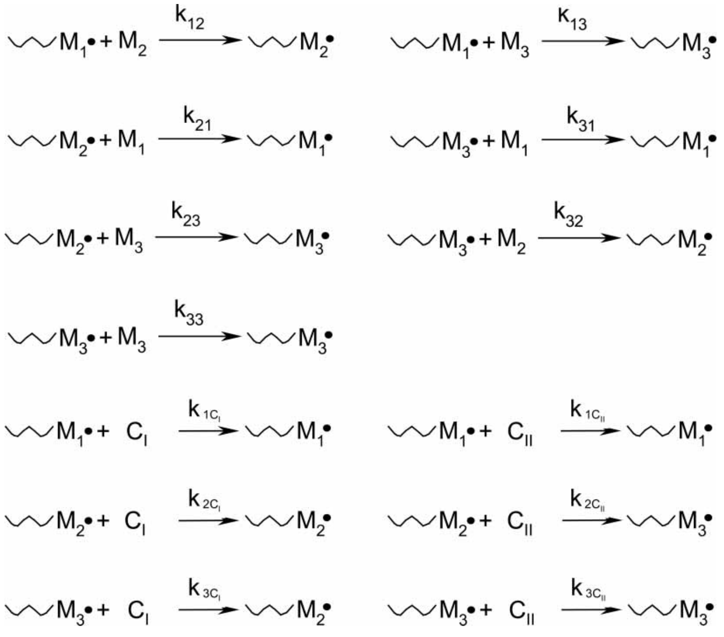
$$A'(X) = \frac{(2k_{12} + k_{22}(k_{12}/k_{21})X)Xv_i^{0.5}}{(k_{t11} + 2k_{t12}(k_{12}/k_{21})X + k_{t22}((k_{12}/k_{21})X)^2)^{0.5}} \tag{19}$$

$$F'(X) = K_1\left(\frac{2k_{1C_I} + 2k_{2C_I}(k_{12}/k_{21})X}{2k_{12} + k_{22}(k_{12}/k_{21})X}\right) \tag{20}$$

In the case that the monomer ratio in the monomer feed X and the chain initiation rate v_i (determined by the initiator concentration) are constant for a series of copolymerizations, A′(X) and F′(X) are also kept constant. Except for the A′(X) and F′(X) formula, polymerization rates (Equations 16–20) have the same forms as the ones of the copolymerization of two non-homopolymerizable monomers (Equations 1–5). Insertion of $k_{22} = 0$ (M_2 is non-homopolymerizable) in Equations 19 and 20, A′(X) and F′(X) become the same values as A(X) and F(X) in Equations 4 and 5.

Terpolymerization of Systems with One Homopolymerizable Monomer

For the terpolymerization of M_1, M_2 and M_3, where M_1 and M_2 are non-homopolymerizable and M_3 is homopolymerizable, as well as C_I and C_{II} are the charge-transfer complexes from M_1/M_2, respectively. M_1/M_3, there are thirteen chain propagation steps:



If the acceptor/donor monomer ratios $X_1 = (M_2)/(M_1)$ and $X_2 = (M_3)/(M_1)$ in monomer feeds, as well as the chain initiation rate v_i (initiator concentration) are constant and with steady state conditions, similar treatment as in the case of binary copolymerizations gives the polymerization rate equation for the ternary system with participation of one homopolymerizable monomer M_3 (Equations 21–28):

$$v_{br} = A'(X_1, X_2)[M_1] + A'(X_1, X_2)F'(X_1, X_2)[M_1]^2 \tag{21}$$

$$v_f = A'(X_1, X_2)[M_1] \tag{22}$$

$$v_{CT} = A'(X_1, X_2)F'(X_1, X_2)[M_1]^2 \tag{23}$$

$$A'(X_1, X_2) = (k_{12}X_1 + k_{13}X_2 + ak_{21} + ak_{23}X_2 + bk_{31} + bk_{32}X_1 + bk_{33}X_2)c \tag{24}$$

$$F'(X_1, X_2) = \frac{2(k_{1C_I}K_1X_1 + k_{1C_{II}}K_2X_2 + ak_{2C_I}K_1X_1 + ak_{2C_{II}}K_2X_2 + bk_{3C_I}K_1X_1 + bk_{3C_{II}}K_2X_2)}{k_{12}X_1 + k_{13}X_2 + ak_{21} + ak_{23}X_2 + bk_{31} + bk_{32}X_1 + bk_{33}X_2} \tag{25}$$

$$a = \frac{k_{12}k_{32}X_1 + k_{13}k_{32}X_2 + k_{12}k_{31}}{k_{21}k_{31}(1/X_1) + k_{23}k_{31}(X_2/X_1) + k_{21}k_{32}} \tag{26}$$

$$b = \frac{k_{12}k_{23}X_1 + k_{13}k_{23}X_2 + k_{13}k_{21}}{k_{21}k_{31}(1/X_2) + k_{21}k_{32}(X_1/X_2) + k_{23}k_{31}} \tag{27}$$

$$c = \left(\frac{v_i}{k_{t11} + a^2k_{t22} + b^2k_{t33} + 2ak_{t12} + 2bk_{t13} + 2abk_{t23}}\right)^{0.5} \tag{28}$$

Both in the case of binary copolymerization and terpolymerization, the total polymerization rate is the sum of two partial polymerization rates of free monomers and of formed charge-transfer complexes, independent of the presence of a homopolymerizable monomer. The partial rate of free monomers is directly proportional to the monomer concentration, and one of the charge-transfer complexes has the proportionality of a second order. Keeping the acceptor/donor monomer ratios and initiator concentration in monomer feeds constant, from the overall polymerization rates at different monomer concentrations, the constants A(A′) and F(F′) can be calculated, so that the participation of free monomers and the formed charge-transfer complexes can be estimated.

Experimental

Materials

MSA (Acros) (50°C/0.08 mbar, m.p. 57.0°C) and NEMI (Acros, 99+%) (40°C/0.08 mbar, m.p. 45°C) were purified by sublimation under reduced pressure. Trans-anethole (Acros, 99%) was fractionally distilled over a 20 cm column under reduced pressure (b.p. 78.0°C/0.8 mbar).

AIBN was recrystallized twice from absolute ethanol and dried under vacuum. THF (Fa. Acros, 99.8% for HPLC) and $CHCl_3$ (Fa. Acros, 99.8% for HPLC) was used without further purification. Diethyl ether was used with the purity for synthesis 0.1 N NaOH and 0.1 N HCl were employed as a standard solution from Merck AG.

Determination of the Equilibrium Constants

The equilibrium constants for the formation of the CT-complexes between ANE and MSA or NEMI were determined in deuterated tetrahydrofuran and chloroform with the ^{1}H-NMR method by Hanna and Ashbaugh (11).

Polymerization Procedure

In 50 mL Schlenk tubes, monomers, AIBN and a solvent were introduced. After three freeze-pump-thaw cycles, the monomer mixtures were polymerized under nitrogen at 60°C. After polymerization, the polymers were obtained by precipitation in a tenfold volume excess of diethyl ether. The precipitated polymers were dried, dissolved in THF, and precipitated in diethyl ether again. The polymers were isolated and dried under vacuum at 40°C until the weight was constant. The polymerization rate was determined gravimetrically, and at all the polymerisations, the conversions were kept below 10 wt%.

Determination of Composition of Polymers

The NEMI unit fraction in the polymers was calculated from the nitrogen contents determined by N-microanalysis. The amount of ANE was determined by UV/VIS spectroscopy at 277 nm (1). MSA in the polymers was calculated from the carboxylic acid group by titration of the hydrolyzed products from about 100 to 200 mg of the polymers. To that, the polymers were hydrolyzed with 5 mL 0.1 N NaOH aqua solution in 50 mL THF under reflux for 1 h. The homogeneous solution was titrated with 0.1 N NaOH or back titrated with 0.1 N HCl in the case of excessive NaOH until neutral. Thymol blue was used as an indicator.

Results and Discussion

From Homopolymerization to Terpolymerization

To complete the polymerizations of the investigated system, the homopolymerizations and the binary copolymerizations of the used monomers were studied. The experiments were carried out under the same conditions as those for the terpolymerization. Even after 20 h of reaction time, no homopolymerization of ANE or MSA was observed. The homopolymerization of NEMI in THF and $CHCl_3$ gave polymers as white powders. The GPC-profile shows that the poly(NEMI) from THF(10^3 g/mol) has lower molar weight than that from $CHCl_3$ (10^5 g/mol). Chain transfer of the active center to the solvent THF (12) seems to be stronger than that to $CHCl_3$. Figure 1 shows the MALDI-TOF spectrum of poly(NEMI) from THF, and the mass/charge-peaks stand one by one with the same distance of 125 Daltons (molar mass of NEMI). This indicates that NEMI really was polymerized without change in its chemical unit.

The poly(NEMI) is soluble in THF and shows a glass temperature at 191°C. The FTIR (1774 cm^{-1}, 1691 cm^{-1}, 1446 cm^{-1}, 1407 cm^{-1}, 1380 cm^{-1}, 1352 cm^{-1}, 1226 cm^{-1}, 1128 cm^{-1}, 659 cm^{-1}) and ^{1}H-NMR (3.4 ppm (CH_2), 1.8 ppm (CH), 1.0 ppm (CH_3)) confirm the polymer structure, the C=C-double bond (FTIR: 1584 cm^{-1}, 830 cm^{-1}, 698 cm^{-1} and ^{1}H-NMR: 6.6 ppm) in the NEMI-monomer disappeared during the polymerization.

The copolymerizations of the binary systems ANE/MSA, ANE/NEMI and MSA/NEMI in THF and in $CHCl_3$ are shown in Tables 1–3. The reactivity ratios were determined by fitting the experimental copolymer compositions and monomer feeds to the copolymerization equation:

$$\frac{\phi_1}{\phi_2} = \frac{\Phi_1}{\Phi_2}\frac{r_1\Phi_1 + \Phi_2}{\Phi_1 + r_2\Phi_2} \tag{29}$$

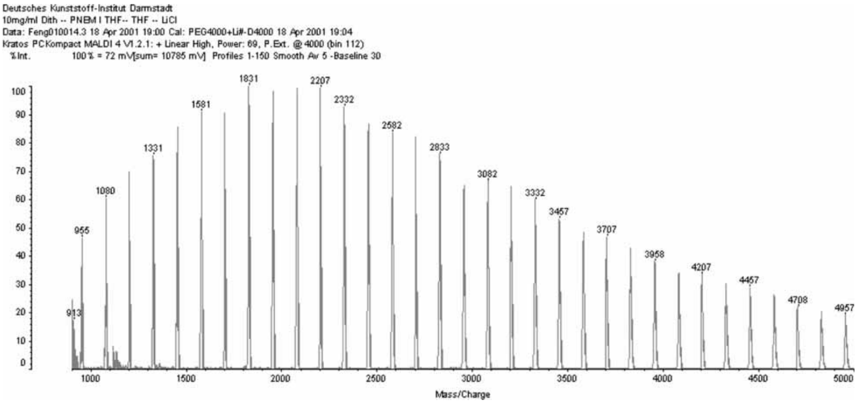


Figure 1. MALDI-TOF diagram of poly(NEMI) from THF.

The copolymerization of the binary system ANE/MSA in $CHCl_3$ is described in another paper (13) together with the system MSA/ANE/vinyl iso-butyl ether. The copolymerization diagrams (Figure 2) show that the copolymerization of ANE/MSA takes place alternately. In the systems ANE/NEMI and MSA/NEMI, the monomers, especially NEMI, show obvious homopolymerizability.

Table 1
Monomer feeds (Φ_i) and copolymer compositions (ϕ_i) of the binary system ANE/MSA in THF at 60°C with AIBN as initiator

Φ_{ANE}	Φ_{MSA}	ϕ_{ANE}	ϕ_{MSA}	r_1	r_2
0.200	0.800	0.499	0.501	0.002	0.001
0.400	0.600	0.499	0.501		
0.600	0.400	0.500	0.500		
0.800	0.200	0.502	0.498		

Table 2
Monomer feeds (Φ_i) and copolymer compositions (ϕ_i) of the binary system ANE/NEMI in $CHCl_3$ and in THF at 60°C with AIBN as initiator

Solvent	Φ_{ANE}	Φ_{NEMI}	ϕ_{ANE}	ϕ_{NEMI}	r_1	r_2
THF	0.226	0.775	0.339	0.661	0.033	0.248
	0.437	0.563	0.427	0.573		
	0.636	0.364	0.478	0.522		
	0.823	0.177	0.521	0.479		
$CHCl_3$	0.224	0.776	0.434	0.566	0.079	0.097
	0.435	0.565	0.485	0.515		
	0.634	0.366	0.517	0.483		
	0.822	0.178	0.573	0.427		

Table 3

Monomer feeds (Φ_i) and copolymer compositions (ϕ_i) of the binary system MSA/NEMI in $CHCl_3$ and in THF at 60°C with AIBN as initiator

Solvent	Φ_{MSA}	Φ_{NEMI}	ϕ_{MSA}	ϕ_{NEMI}	r_1	r_2
THF	0.196	0.804	0.148	0.852	0.158	1.676
	0.407	0.593	0.236	0.764		
	0.509	0.491	0.294	0.706		
	0.503	0.497	0.301	0.699		
	0.798	0.202	0.538	0.462		
$CHCl_3$	0.221	0.779	0.104	0.896	0.070	2.677
	0.487	0.513	0.214	0.786		
	0.592	0.408	0.279	0.721		
	0.725	0.275	0.360	0.640		
	0.805	0.195	0.446	0.554		

The terpolymerizations of ANE, MSA and NEMI in THF and $CHCl_3$ are shown in Tables 4 and 5. Together with the binary copolymerizations, they can be described in a Slocombe-diagram (14). In the triangle diagram, each arrow describes a polymerization result. It starts at the monomer feed and ends at the polymer composition of the resulting polymer. As an example, the terpolymerization of ANE, MSA and NEMI in $CHCl_3$ shows the Slocombe-diagram in Figure 3.

The resulting terpolymers contain more acceptor monomer units than donor monomer units. This agrees with the homopolymerizability of NEMI, but the arrows are always directed to the ANE/MSA side, which indicates a stronger copolymerizability of MSA

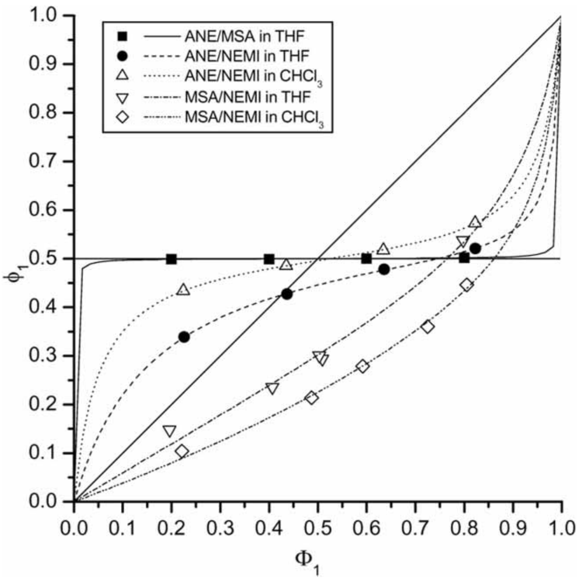


Figure 2. Copolymerization diagrams of ANE/MSA, ANE/NEMI and MSA/NEMI in THF and in CHCl3 at 60°C with AIBN as initiator.

Table 4
Monomer feeds (Φ_i) and copolymer compositions (ϕ_i) of the ternary system ANE/MSA/NEMI in THF at 60°C with AIBN as initiator

Φ_{ANE}	Φ_{MSA}	Φ_{NEMI}	ϕ_{ANE}	ϕ_{MSA}	ϕ_{NEMI}
0.513	0.260	0.227	0.406	0.339	0.255
0.524	0.199	0.278	0.377	0.297	0.326
0.492	0.324	0.184	0.407	0.390	0.203
0.505	0.108	0.387	0.357	0.230	0.413
0.488	0.419	0.094	0.345	0.554	0.100
0.102	0.477	0.421	0.313	0.338	0.348
0.296	0.374	0.330	0.379	0.338	0.283
0.504	0.263	0.233	0.363	0.381	0.256
0.621	0.202	0.178	0.433	0.309	0.258
0.715	0.152	0.134	0.484	0.264	0.253
0.769	0.123	0.109	0.439	0.322	0.239
0.806	0.103	0.091	0.461	0.296	0.244

than that of NEMI against the free ANE-radical. In both solvents, the monomers show similar reactivities and so tetrahydrofuran and chloroform have only weak solvent effects on the polymer composition.

Kinetic Measurements

According to the model of simultaneous participation of free monomers and charge-transfer complexes, both species participate parallel in the polymerization process. The participation of the two kinds of species can be estimated via kinetic measurements.

Table 5
Monomer feeds (Φ_i) and copolymer compositions (ϕ_i) of the ternary system ANE/MSA/NEMI in $CHCl_3$ at 60°C with AIBN as initiator

Φ_{ANE}	Φ_{MSA}	Φ_{NEMI}	ϕ_{ANE}	ϕ_{MSA}	ϕ_{NEMI}
0.520	0.248	0.232	0.420	0.362	0.219
0.512	0.204	0.284	0.422	0.315	0.263
0.511	0.309	0.180	0.412	0.432	0.156
0.533	0.102	0.366	0.365	0.291	0.345
0.517	0.395	0.089	0.405	0.522	0.073
0.096	0.478	0.426	0.381	0.355	0.264
0.294	0.374	0.333	0.444	0.343	0.213
0.504	0.262	0.234	0.453	0.341	0.206
0.628	0.197	0.175	0.451	0.338	0.211
0.727	0.144	0.129	0.468	0.321	0.211
0.764	0.125	0.111	0.463	0.324	0.212
0.505	0.262	0.233	0.458	0.333	0.209

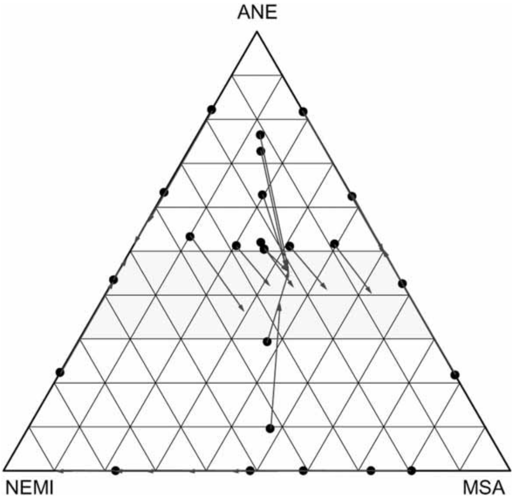


Figure 3. Slocombe diagram of the ternary system ANE/MSA/NEMI in $CHCl_3$ at 60°C with AIBN as initiator.

For that purpose, the overall polymerization rate of binary copolymerization and terpolymerization with different monomer concentration at constant acceptor/donor monomer ratios, as well as AIBN concentration have been determined (Tables 6–10).

Table 6

Kinetic measurements of the system ANE/MSA (K = 0.12) in THF at 60°C and varying $X = [MSA]/[ANE]$ with AIBN as initiator $[AIBN] = 1.58 \times 10^{-3}$ mol/L

$X =$ $[MSA]/[ANE]$	[ANE] [mol/L]	v_{br} [mol/L/s]	A(X)	F(X)	$[ANE]_c$ [mol/L]
0.2500	1.2800	5.0507×10^{-6}	2.7×10^{-6}	1.5	0.21
	0.8000	2.3511×10^{-6}			
	0.3200	4.2271×10^{-7}			
	0.1600	1.1960×10^{-8}			
0.6667	0.9600	1.0184×10^{-5}	5.8×10^{-6}	1.1	0.90
	0.7200	4.9512×10^{-6}			
	0.4800	4.4031×10^{-6}			
	0.2400	1.5725×10^{-6}			
1.5000	0.6400	1.4941×10^{-5}	1.0×10^{-5}	2.0	0.50
	0.4800	1.0154×10^{-5}			
	0.3200	5.9857×10^{-6}			
	0.1600	2.1096×10^{-6}			
4.0001	0.3200	2.0350×10^{-5}	2.0×10^{-5}	7.5	0.13
	0.2000	1.0121×10^{-5}			
	0.0800	2.9017×10^{-6}			
	0.0400	7.0845×10^{-7}			

Table 7
Kinetic measurements of the system ANE/NEMI (K = 0.07) in THF at 60°C and varying $X = [NEMI]/[ANE]$ with AIBN as initiator [AIBN] = 2.03×10^{-3} mol/L

$X =$ $[NEMI]/[ANE]$	[ANE] [mol/L]	v_{br} [mol/L/s]	$A'(X)$ [s^{-1}]	$F'(X)$ [L/mol]	$[ANE]_c$ [mol/L]
0.5775	1.0150	2.8602×10^{-5}	6.9×10^{-6}	2.9	0.35
	0.7612	1.9497×10^{-5}			
	0.5075	1.1009×10^{-5}			
	0.2537	2.5843×10^{-6}			
1.2993	0.6767	3.8109×10^{-5}	9.8×10^{-6}	7.1	0.14
	0.5075	2.5521×10^{-5}			
	0.3383	1.3906×10^{-5}			
	0.1692	2.9467×10^{-6}			
0.2166	1.3533	1.5247×10^{-5}	5.6×10^{-7}	15.1	0.07
	0.8458	7.3580×10^{-6}			
	0.3383	1.1794×10^{-6}			
	0.1692	2.4256×10^{-7}			
3.4649	0.3383	4.5652×10^{-5}	1.0×10^{-5}	43.0	0.02
	0.2115	2.2193×10^{-5}			
	0.0846	2.0448×10^{-6}			
	0.0423	7.8113×10^{-8}			

Table 8
Kinetic measurements of the system ANE/NEMI (K = 0.04) in $CHCl_3$ at 60°C and varying $X = [NEMI]/[ANE]$ with AIBN as initiator [AIBN] = 1.97×10^{-3} mol/L

$X =$ [NEMI]/[ANE]	[ANE] [mol/L]	v_{br} [mol/L/s]	$A'(X)$ [s^{-1}]	$F'(X)$ [L/mol]	$[ANE]_c$ [mol/L]
0.5725	1.0261	4.0227×10^{-5}	2.0×10^{-5}	1.0	1.00
	0.7695	3.0353×10^{-5}			
	0.5130	1.8160×10^{-5}			
	0.2565	7.0059×10^{-6}			
1.2882	0.6840	5.3457×10^{-5}	4.0×10^{-5}	1.5	0.67
	0.5130	3.6096×10^{-5}			
	0.3420	2.3405×10^{-5}			
	0.1710	7.4676×10^{-6}			
0.2147	1.3681	2.1382×10^{-5}	3.4×10^{-6}	2.9	0.35
	0.8550	1.1386×10^{-5}			
	0.3420	2.7556×10^{-6}			
	0.1710	5.4300×10^{-7}			
3.4352	0.3420	5.2610×10^{-5}	9.0×10^{-5}	2.3	0.43
	0.2138	3.2049×10^{-5}			
	0.0855	1.0038×10^{-5}			
	0.0428	3.7916×10^{-6}			

Table 9
Kinetic measurements of the system ANE/MSA/NEMI in THF at 60°C and varying $X_1 = [MSA]/[ANE]$ and $X_2 = [NEMI]/[ANE]$ with AIBN as initiator

[ANE][mol/L]	v_{br} [mol/L/s]	V_{br}/[ANE] [s^{-1}]
0.9307	3.7084×10^{-5}	3.9844×10^{-5}
0.5584	1.8775×10^{-5}	3.3621×10^{-5}
0.4654	1.4580×10^{-5}	3.1331×10^{-5}
0.2327	4.4844×10^{-6}	1.9272×10^{-5}
[AIBN] = 1.8971×10^{-3} (mol/L), $X_1 = 0.2147$, $X_2 = 0.7668$		
$A'(X_1,X_2) = 1.5\times10^{-5}$, $F'(X_1,X_2) = 2.0$, $[ANE]_c = 0.50$ (mol/L)		
1.1039	4.2690×10^{-5}	3.8673×10^{-5}
0.8279	2.8251×10^{-5}	3.4123×10^{-5}
0.5519	1.5971×10^{-5}	2.8936×10^{-5}
0.4140	7.8598×10^{-6}	1.8987×10^{-5}
0.2760	6.3980×10^{-6}	2.3184×10^{-5}
[AIBN] = 1.8396×10^{-3} (mol/L), $X_1 = 0.3797$, $X_2 = 0.5298$		
$A'(X_1,X_2) = 1.2\times10^{-5}$, $F'(X_1,X_2) = 2.2$, $[ANE]_c = 0.46$ (mol/L)		
0.9790	2.9881×10^{-5}	3.0522×10^{-5}
0.8159	2.3027×10^{-5}	2.8223×10^{-5}
0.6527	1.7333×10^{-5}	2.6556×10^{-5}
0.4895	1.1842×10^{-5}	2.4191×10^{-5}
0.4079	9.2562×10^{-6}	2.2692×10^{-5}
0.3264	6.9650×10^{-6}	2.1339×10^{-5}
0.2448	3.6075×10^{-6}	1.4736×10^{-5}
0.1632	2.6967×10^{-6}	1.6524×10^{-5}
[AIBN] = 1.9117×10^{-3} (mol/L), $X_1 = 0.5062$, $X_2 = 0.4426$		
$A'(X_1,X_2) = 1.3\times10^{-5}$, $F'(X_1,X_2) = 1.5$, $[ANE]_c = 0.69$ (mol/L)		
1.0259	3.1303×10^{-5}	3.0511×10^{-5}
0.7695	2.2198×10^{-5}	2.8850×10^{-5}
0.5130	1.3423×10^{-5}	2.6166×10^{-5}
0.3847	9.7102×10^{-6}	2.5239×10^{-5}
0.2565	5.6515×10^{-6}	2.2034×10^{-5}
[AIBN] = 1.8172×10^{-3} (mol/L), $X_1 = 0.6592$, $X_2 = 0.3744$		
$A'(X_1,X_2) = 2.0\times10^{-5}$, $F'(X_1,X_2) = 0.5$, $[ANE]_c = 2.01$ (mol/L)		
0.9307	2.5147×10^{-5}	2.7018×10^{-5}
0.5584	1.2606×10^{-5}	2.2573×10^{-5}
0.4654	1.0908×10^{-5}	2.3440×10^{-5}
0.2327	3.8394×10^{-6}	1.6500×10^{-5}
[AIBN] = 1.8971×10^{-3} (mol/L), $X_1 = 0.8587$, $X_2 = 0.1917$		
$A'(X_1,X_2) = 1.2\times10^{-5}$, $F'(X_1,X_2) = 1.5$, $[ANE]_c = 0.67$ (mol/L)		

Typical courses for the monomer concentration dependence of the overall polymerization rate of the two binary systems and the ternary system in THF and $CHCl_3$ are shown in Figures 4–6.

Fittings of Equations 1, 16, and 21 to the overall polymerization rates for the systems ANE/MSA, ANE/NEMI and ANE/MSA/NEMI give the factors A(X), A′(X),

Table 10

Kinetic measurements of the system ANE/MSA/NEMI in $CHCl_3$ at 60°C and varying $X_1 = [MSA]/[ANE]$ and $X_2 = [NEMI]/[ANE]$ with AIBN as initiator

[ANE][mol/L]	v_{br} [mol/L/s]	v_{br}/[ANE] [s^{-1}]
0.8622	3.2259×10^{-5}	3.7416×10^{-5}
0.5173	1.7499×10^{-5}	3.3828×10^{-5}
0.4311	1.5464×10^{-5}	3.5872×10^{-5}
0.2155	6.2479×10^{-6}	2.8987×10^{-5}
[AIBN] = 1.7831×10^{-3} (mol/L), $X_1 = 0.1912$, $X_2 = 0.6862$ $A'(X_1,X_2) = 3.0 \times 10^{-5}$, $F'(X_1,X_2) = 0.3$, $[ANE]_c = 3.00$ (mol/L)		
1.0622	4.4872×10^{-5}	4.2244×10^{-5}
0.7967	3.2617×10^{-5}	4.0942×10^{-5}
0.5311	2.1559×10^{-5}	4.0593×10^{-5}
0.3983	1.4763×10^{-5}	3.7063×10^{-5}
0.2656	8.8927×10^{-6}	3.3488×10^{-5}
0.1328	3.5872×10^{-6}	2.7017×10^{-5}
[AIBN] = 2.0401×10^{-3} (mol/L), $X_1 = 0.3980$, $X_2 = 0.5554$ $A'(X_1,X_2) = 3.0 \times 10^{-5}$, $F'(X_1,X_2) = 0.4$, $[ANE]_c = 2.32$ (mol/L)		
1.0160	3.3995×10^{-5}	3.3460×10^{-5}
0.8467	2.8027×10^{-5}	3.3102×10^{-5}
0.6773	2.2812×10^{-5}	3.3679×10^{-5}
0.5080	1.5972×10^{-5}	3.1440×10^{-5}
0.4233	1.3534×10^{-5}	3.1970×10^{-5}
0.3387	1.1300×10^{-5}	3.3367×10^{-5}
0.2540	4.7740×10^{-6}	1.8795×10^{-5}
0.1693	4.5071×10^{-6}	2.6617×10^{-5}
[AIBN] = 1.9400×10^{-3} (mol/L), $X_1 = 0.4769$, $X_2 = 0.4472$ $A'(X_1,X_2) = 2.5 \times 10^{-5}$, $F'(X_1,X_2) = 0.5$, $[ANE]_c = 2.08$ (mol/L)		
1.0632	3.2922×10^{-5}	3.0963×10^{-5}
0.7974	2.4072×10^{-5}	3.0186×10^{-5}
0.5316	1.5562×10^{-5}	2.9272×10^{-5}
0.3987	1.1669×10^{-5}	2.9267×10^{-5}
0.2658	7.0560×10^{-6}	2.6545×10^{-5}
[AIBN] = 1.8493×10^{-3} (mol/L), $X_1 = 0.6053$, $X_2 = 0.3519$ $A'(X_1,X_2) = 2.6 \times 10^{-5}$, $F'(X_1,X_2) = 0.2$, $[ANE]_c = 5.68$ (mol/L)		
0.8622	2.3231×10^{-5}	2.6945×10^{-5}
0.5173	1.2627×10^{-5}	2.4409×10^{-5}
0.4311	1.0578×10^{-5}	2.4538×10^{-5}
0.2155	4.6386×10^{-6}	2.1521×10^{-5}
[AIBN] = 1.7812×10^{-3} (mol/L), $X_1 = 0.7647$, $X_2 = 0.1716$ $A'(X_1,X_2) = 2.0 \times 10^{-5}$, $F'(X_1,X_2) = 0.4$, $[ANE]_c = 2.51$ (mol/L)		

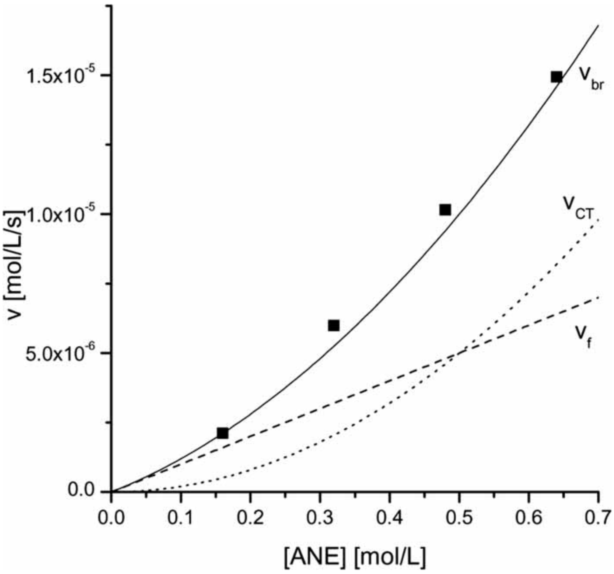


Figure 4. Polymerization rate in dependence on the monomer concentration of the binary system ANE/MSA (X = [MSA]/[ANE] = 1.500, [AIBN] = 1.58×10^{-3}mol/L) in THF at 60°C.

A′(X_1,X_2), F(X), F′(X) and F′(X_1,X_2), with which the partial polymerization rates of free monomers and the ones of CT-complexes can be calculated. They have been plotted in the diagrams. All the diagrams show a similar shape. At low monomer concentrations, the free monomers determine the overall polymerization rate. However, the partial rate

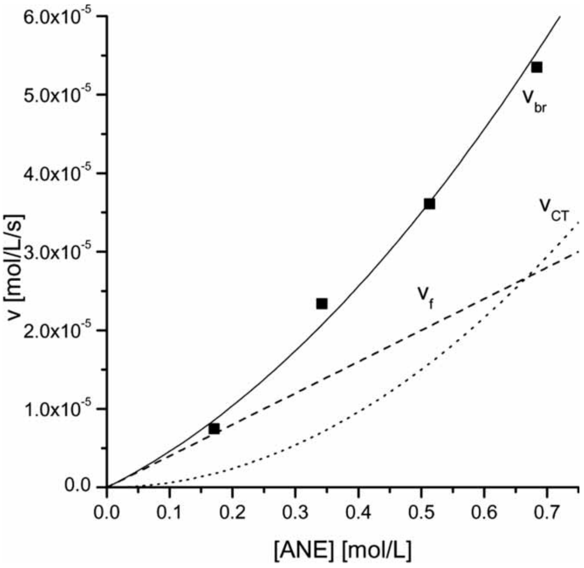


Figure 5. Polymerization rate in dependence on the monomer concentration of the binary system ANE/NEMI (X = [NEMI]/[ANE] = 1.2882, [AIBN] = 1.97×10^{-3}mol/L) in $CHCl_3$ at 60°C.

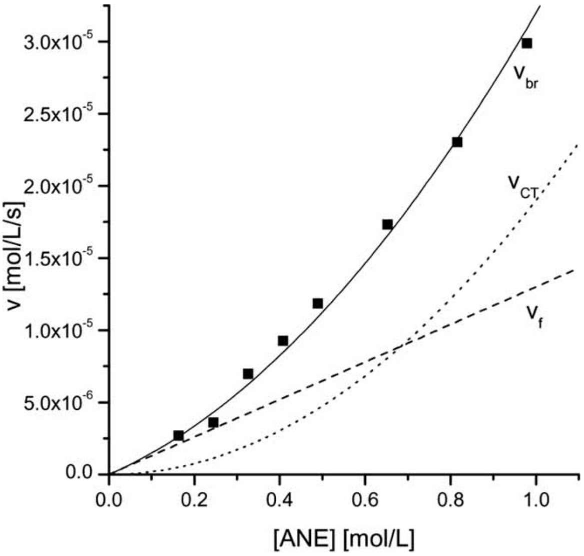


Figure 6. Polymerization rate in dependence on the monomer concentration of the ternary system ANE/MSA/NEMI ($X_1 = [MSA]/[ANE] = 0.5062$, $X_2 = [NEMI]/[ANE] = 0.4426$, $[AIBN] = 1.9117 \times 10^{-3}$mol/L) in THF at 60°C.

of the CT-complexes increases faster with the monomer concentration and turns after the intersection points (critical monomer concentration $(M_1)_c$) into the all-dominant part of the overall polymerization rate. This phenomenon is due to the second order of the polymerization rate in relation to the monomer concentrations (Equations 18 and 23) in the charge-transfer complex model, but only the first order for the free monomer model (Equations 17 and 22). On the other hand, the CT-complexes are generally much more reactive than the free monomers. Comparison of the critical monomer concentration is insignificant, because the polymerizations were carried out at different monomer ratios and here only the donor monomer concentration can be taken into account.

At the same monomer- and initiator concentrations, the polymerization rate depends on the monomer ratios in the feeds. Figures 7–9 show the course of the polymerization rate depending on the donor/acceptor monomer ratios. The polymerization rates were divided by the quadratic root of AIBN concentration.

It can be seen that the polymerization rate increases with the monomer concentrations, and on the other hand, the polymerization rates show maximums. At low monomer concentrations, the maximum is located at a monomer ratio near 1 : 1. With an increase of the monomer concentrations, the maximum of the polymerization rate of the system ANE/MSA in THF and the system ANE/NEMI in both solvents changes to monomer feeds with less ANE. This is incompatible with the CT-complex model. According to the CT-complex model, the complexes should determine the overall polymerization rate progressively with increasing of the monomer concentration, and the maximum complex concentration should appear at the monomer ratio of 1 : 1. For the system ANE/MSA, an explanation is possible by the relative higher reactivity of MSA in THF. MSA takes part in the polymerization process not as a total by free monomer, but in solvated form. The homopolymerizability of NEMI leads to the shifts of the maximum polymerization rate from 1 : 1 at the monomer feed.

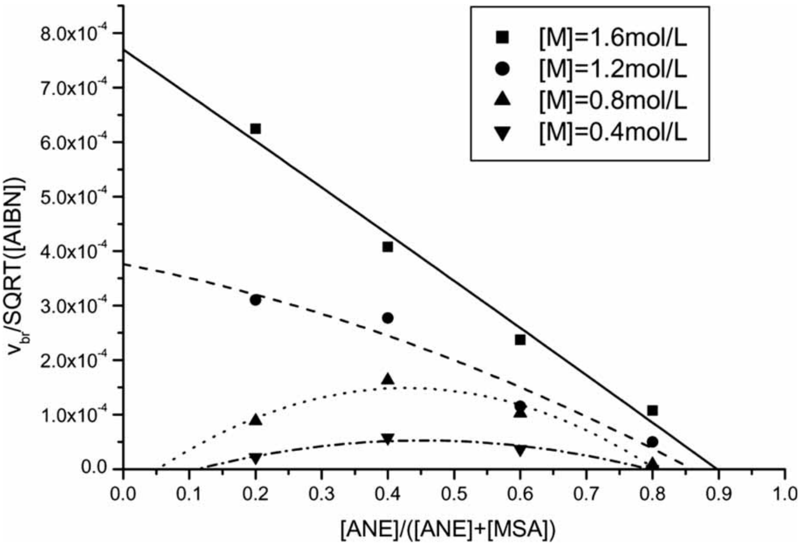


Figure 7. Polymerization rate in dependence on the monomer concentration and monomer ratios of the binary system ANE/MSA in THF at 60°C.

In the system ANE/MSA in THF, the drawing of F(X) against X (Figure 10) gives K_1 (k_{1C_l}/k_{12}) and K_1 (k_{2C_l}/k_{21}), with the known equilibrium constant K_1 the relative reactivity of the CT-complex and the free monomers can be estimated. The fitting of Equation 5 gives $(k_{1C_l}/k_{12}) = 1.87$ and $(k_{2C_l}/k_{21}) = 15.07$. As proposed, the CT-complex has a higher reactivity than the free monomers.

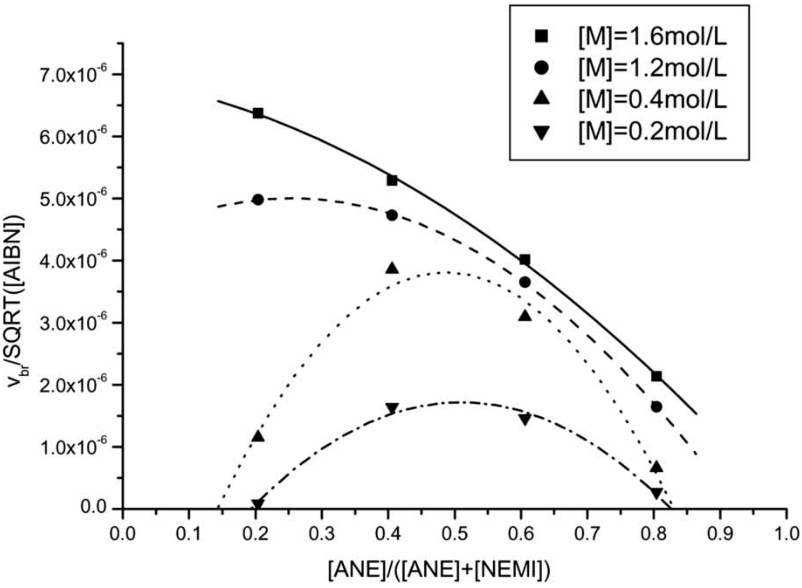


Figure 8. Polymerization rate in dependence on the monomer concentration and monomer ratios of the binary system ANE/NEMI in THF at 60°C.

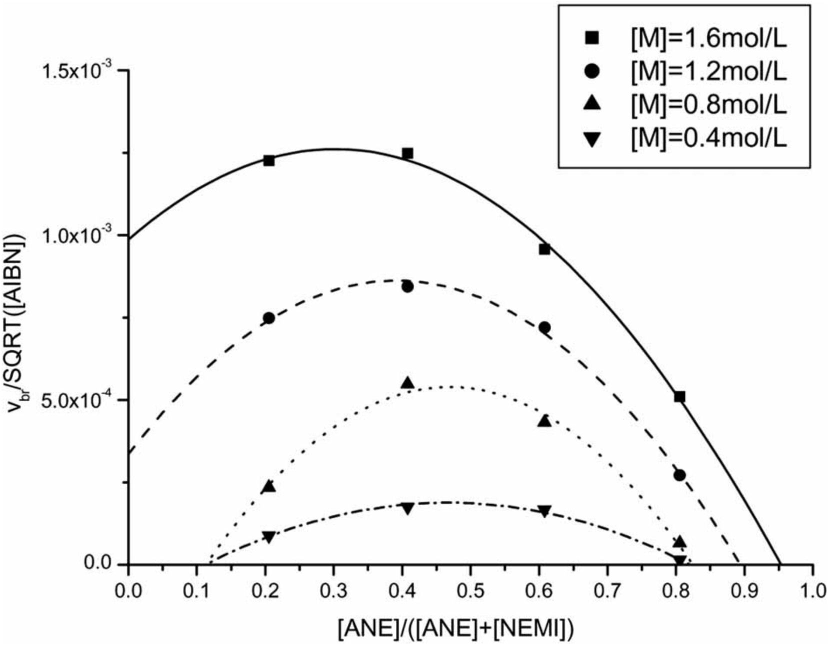


Figure 9. Polymerization rate in dependence on the monomer concentration and monomer ratios of the binary system ANE/NEMI in $CHCl_3$ at 60°C.

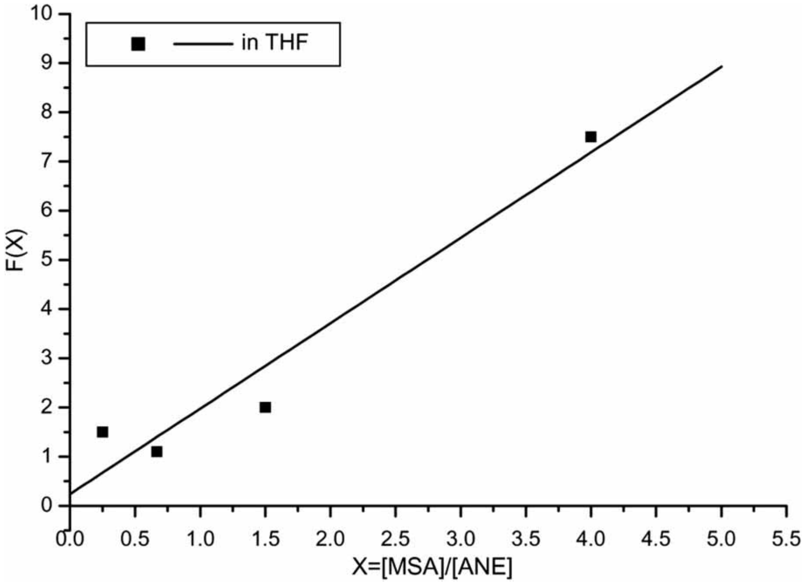


Figure 10. Drawing of F(X) against X for the copolymerization of ANE/MSA in THF at 60°C with AIBN as initiator.

Conclusions

The monomers trans-anethole (ANE) and maleic anhydride (MSA) cannot be free radically homopolymerized in tetrahydrofuran and in chloroform. The homopolymerization of N-ethylmaleimide (NEMI) gives white powder polymers after a long reaction time. ANE/MSA and ANE/NEMI can easily copolymerize in THF and $CHCl_3$ to alternating copolymers. The ternary terpolymerization of ANE, MSA and NEMI results in terpolymers with more than 50 (mol%) MSA + NEMI-units. The polymerization rate of the co- and terpolymerizations show reaction orders between 1 and 2. This is due to the simultaneous participation of free monomers and CT-complexes in the polymerization process. Their contributions can be determined via kinetic measurements. At low monomer concentrations, the free monomers determine the overall polymerization rate. With increase of the monomer concentration the partial rate of the CT-complexes dominates. Near the intersection point of v_{CT} and v_f both the free monomers and the CT-complexes participate to the same extent to the overall polymerization. In the binary copolymerizations, the maximum of the polymerization rate is not always located at the monomer ratio of 1 : 1. With increasing monomer concentrations, the maximum moves progressively to the monomer feed with less trans-anethole.

Acknowledgement

Financial support from Dr. Illing Stiftung is gratefully acknowledged.

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