

Free radical quaterpolymerization of acceptor- and donor-monomers

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Summary

This paper describes first the free radical quaterpolymerization of acceptor-monomers (maleic anhydride (MSA), fumaronitrile (FN) and N-ethylmaleimide (NEMI)) and donor-monomers (trans-anethole (ANE), vinyl-iso-butylether (VIBE), trans-stilbene (Stb) and 2-chloroethyl vinylether (CEVE)). They form quaternary systems from two acceptors and two donors (MSA/FN/ANE/VIBE) as well as from one acceptor and three donors (NEMI/ANE/Stb/CEVE and MSA/ANE/Stb/CEVE). A first time presented quaterpolymerization diagram can describe the relationship between the polymer composition and the monomer feed. The relative reactivities of these monomers were determined. Against the common acceptor macroradical the donor monomer ANE is more reactive than VIBE, Stb and CEVE.

Introduction

During last years free radical copolymerizations of acceptor- and donor-monomers have attracted great interest. Many of these monomers are non-homopolymerizable under free radical conditions but can copolymerize easily, yielding alternating polymers with acceptor- and donor-units and defined chemical structure. They often carry functional groups and enable chemical modifications of the resulting polymers.

The alternating free radical co- and terpolymerizations of acceptors and donors can be described by various models. The terminal-model [1] and the penultimate-model [2] with free monomers as well as the charge-transfer-complex-model [3] can in most cases satisfactorily describe the compositions of the resulting polymers. The model of the simultaneous participation of free monomers and complexes [4] can quantitatively determine their contribution to the overall polymerization rate by kinetic measurements.

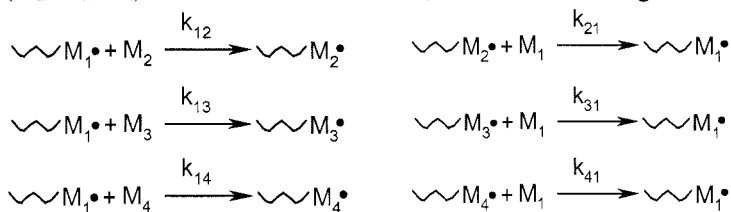
Investigations on systems with more than three acceptor and donor monomers are not reported till now. One reason is the difficulty to describe graphically the compositions of the polymers versus the monomer feeds. In this paper quaternary systems from acceptor- and donor-monomers are studied, which all or some of them are non-homopolymerizable. At the first time a quaterpolymerization diagram is represented to show the resulting polymer compositions in dependence on the monomer feeds.

Maleic anhydride (MSA), fumaronitrile (FN) and N-ethylmaleimide (NEMI) are typical acceptor-monomers. Trans-anethole (ANE), vinyl-iso-butylether (VIBE), trans-stilbene (Stb) and 2-chloroethyl vinylether (CEVE) belong to the group of electron-donors. They were studied in various binary and ternary systems and their

non-homopolymerizability was confirmed except for NEMI [5-7].

Theory

If all the monomers in a quaternary system are non-homopolymerizable and the copolymerization takes place only between monomers of electronically different type, one quaternary system can be composed either from two acceptor- (M_1, M_2) and two donor-monomers (M_3, M_4) or from one acceptor- (M_1) and three donor-monomers (M_2, M_3, M_4) or inverse. In the last case, there are six chain growth steps:



k_{ij} is the rate constant of the reaction of $\sim M_i \cdot$ and M_j

Comparing the amounts of the monomer units M_2, M_3 and M_4 in the polymers (ϕ_i) with their amounts in the monomer feeds (Φ_i) results in their relative reactivity with the common macroradical $\sim M_1 \cdot$ (eq. 1):

$$\frac{\phi_2}{\Phi_2} : \frac{\phi_3}{\Phi_3} : \frac{\phi_4}{\Phi_4} = k_{12} : k_{13} : k_{14} \quad \text{eq. 1}$$

Experimental

Materials

Maleic anhydride (Acros), fumaronitrile (Acros) and N-ethylmaleimide (Acros, 99+%) were purified by sublimation under reduced pressure (0.1 mbar, 50°C). Sublimation of trans-stilben was carried out at 0.07 mbar and 115°C. Trans-anethole (Acros, 99%), vinyl-iso-butylether (Fluka, 99%) and 2-chloroethyl vinylether (Acros, 95%) were fractionally distilled over a 20 cm column. α, α' -azoisobutyronitrile (AIBN) was twice recrystallized from absolute ethanol and dried in vacuum over calcium chloride. The solvents chloroform (HPLC, Acros) and tetrahydrofuran (Acros, 99.8% for HPLC) were employed without further purification.

Polymerization

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 in tetrahydrofuran or in chloroform. 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 anhydrous diethyl ether. The precipitated polymers were dried, dissolved in tetrahydrofuran and precipitated in diethyl ether once again and dried under reduced pressure at 40°C to constant weight. In all the polymerizations the

conversions were kept below 10 wt-%.

Characterization

The quaterpolymers were characterized by FT-IR (KBr-disc, FTIR-8101M, Shimadzu), $^1\text{H-NMR}$ (in DMSO- d_6 , WM 300, Bruker), GPC (THF as eluent, HPGPC, Waters, PS-standard) and DSC (10 °C/min under N_2 , 912 DS-DSC, DuPont), etc. The amounts of ANE units were determined by UV/VIS-spectroscopy (Specord 200, Analytik Jena) at 277 nm. The FN and NEMI units were determined by nitrogen microanalysis. CEVE units were determined by chlorine elemental analysis. The MSA units were determined by hydrolysis-titration in THF with 0.1 N standard NaOH solution [6].

Results and discussion

1. Characterization

FTIR (KBr-disc): 1780/1861 cm^{-1} ($\nu_{\text{C=O}}$ of MSA), 1697/1771 cm^{-1} ($\nu_{\text{C=O}}$ of NEMI), 2247 cm^{-1} ($\nu_{\text{C}\equiv\text{N}}$ of FN), 1514/1610 cm^{-1} ($\delta_{\text{C=C}}$ of ANE), 1099 cm^{-1} ($\delta_{\text{C-O}}$ of VIBE), 665 cm^{-1} ($\nu_{\text{C-Cl}}$ of CEVE).

$^1\text{H-NMR}$ (DMSO- d_6): 6 - 8 ppm (arom. protons of ANE and Stb), 3.7 ppm (OCH_3 of ANE), 0.5 - 1 ppm (alkyl protons of NEMI and VIBE), MSA and FN units show very weak chemical shifts.

UV/VIS (1,2-dichloroethane): 230 nm, 277 nm and 285 nm (ANE).

The quaterpolymers show monomodal distributions of the molecular weights ($M_n = 10^3$ - 10^5 g/mol) in GPC-measurements. Very interesting is that for all three systems the polymers from chloroform have higher molecular weights than those from tetrahydrofuran. It is well known that chloroform is a good chain transfer agent. But in the polymerization of some polar monomers the transfer to tetrahydrofuran is the most important step for a chain start [8].

According to the DSC-measurements the polymers from the systems MSA/FN/ANE/VIBE ($\sim 185^\circ\text{C}$), MSA/ANE/Stb/CEVE ($\sim 213^\circ\text{C}$) and NEMI/ANE/Stb/CEVE ($\sim 217^\circ\text{C}$) show only one relatively high glass temperature due to the high polarities and the stiffness of the monomer-units in the polymers. With similar polymer composition poly(NEMI-ANE-Stb-CEVE) has a little higher glass temperature than poly(MSA-ANE-Stb-CEVE), probably because the NEMI-unit is larger than the MSA-unit and prevents chain rotation. The glass temperatures vary with the polymer composition.

2. Quaterpolymerization diagrams

To visualize copolymerizations, conventional copolymerization diagrams for binary systems and the slocombe-diagram [9] for ternary systems are used. A quaternary system has three independent composition parameters for the monomer feeds and for the resulting polymers, respectively. Therefore, a normal two dimensional diagram is not able to describe the polymerization results. For the first time we propose a method to illustrate the quaterpolymerization with one set of bar charts. The lower diagram gives the compositions of the monomer feeds; the middle one represents the polymer

compositions and the upper one is specially suitable for the polymerization of acceptor- and donor-monomers and illustrates the sum of the acceptor- and the donor-units in the polymers. This method can in principle also be used for other copolymerizations with more monomers. Different is only the number of the bars.

The System MSA/FN/ANE/VIBE

MSA ($e = 2.25$) and FN ($e = 1.96$) are typical acceptor monomers, whereas ANE ($e = -1.4$) and VIBE ($e = -1.77$) are electron donors. All these four monomers are not homopolymerizable and can form a quaternary system of two acceptor- and two donor-monomers. The dependence of the polymer compositions on the monomer feeds is shown in Figure 1 and Figure 2.

It can be seen that the polymer compositions diverge obviously from the monomer feeds but the overall amounts of the two acceptor-units and the two donor-units in the polymers are always nearly the same, independent on the monomer feeds. But the incorporated amounts of the individual acceptor- or donor-monomers are different, depending on their concentrations and reactivities.

The quaterpolymerization diagrams show also that in chloroform the sums of the amounts of the donor-monomer-units are slightly higher than 0.5 (mol fraction) and in tetrahydrofuran just reversed. The reason can be the acceptor or donor character of the used solvents, which may influence the propagation step by complex formation with the monomers.

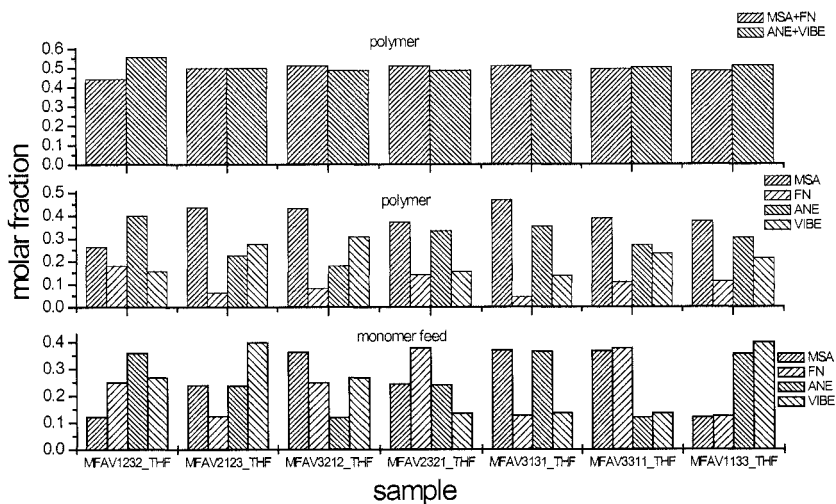


Figure 1. Quaterpolymerization diagram of the system MSA/FN/ANE/VIBE in tetrahydrofuran at 60°C with AIBN as initiator

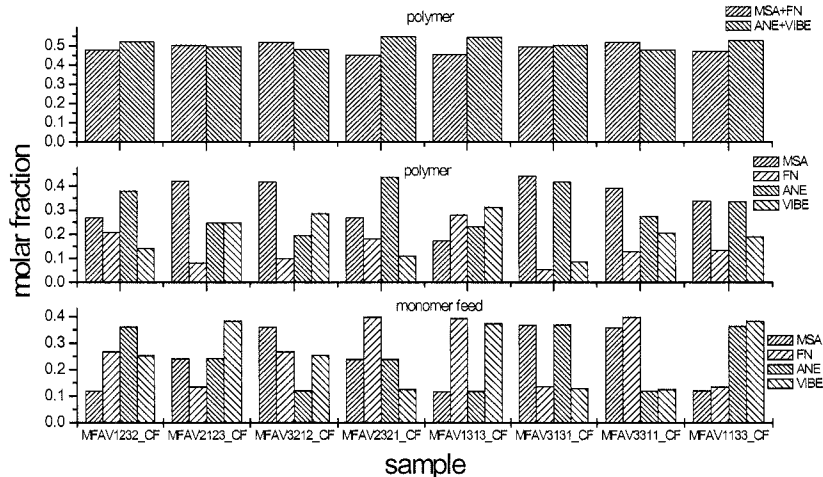


Figure 2. Quaterpolymerization diagram of the system MSA/FN/ANE/VIBE in chloroform at 60°C with AIBN as initiator

The System MSA/ANE/Stb/CEVE

The compositions of the monomer feeds and the resulting polymers for the system MSA/ANE/Stb/CEVE in tetrahydrofuran and in chloroform are shown in the quaterpolymerization diagram (Figure 3). ANE has compared to Stb and CEVE a higher reactivity. But in the quaterpolymers the molar ratios of the MSA and (ANE+Stb+CEVE) units always equal 1, regardless of the monomer feeds and the used solvents.

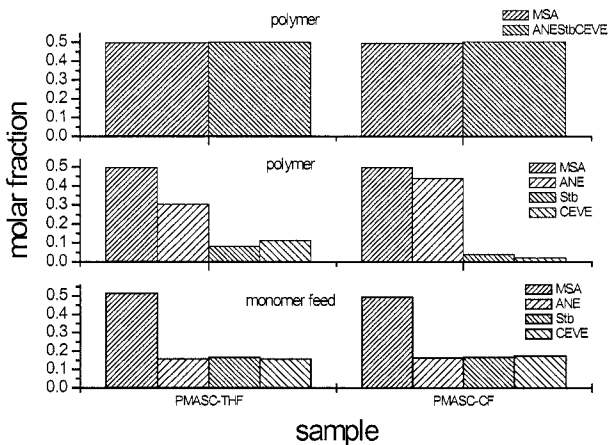


Figure 3. Quaterpolymerization diagram of the system MSA/ANE/Stb/CEVE in tetrahydrofuran and in chloroform at 60°C with AIBN as initiator

The System NEMI/ANE/Stb/CEVE

The quaterpolymerization diagrams for the system NEMI/ANE/Stb/CEVE in tetrahydrofuran and in chloroform are shown in Figure 4 and Figure 5.

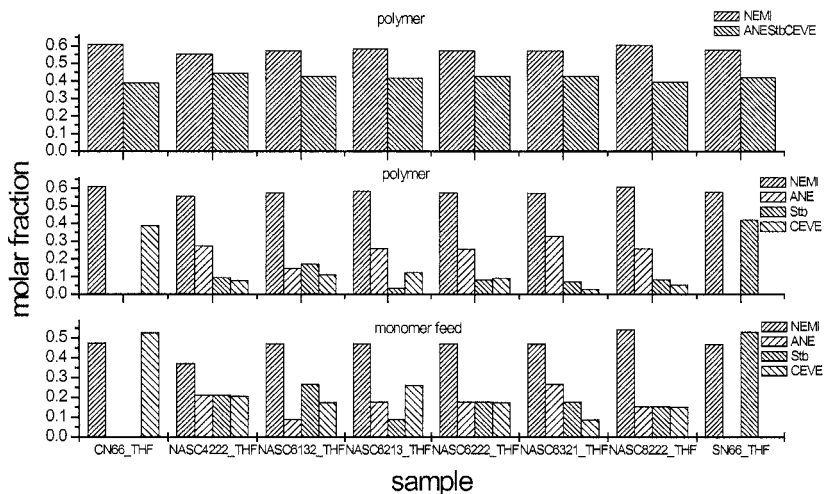


Figure 4. Quaterpolymerization diagram of the system NEMI/ANE/Stb/CEVE in tetrahydrofuran at 60°C with AIBN as initiator

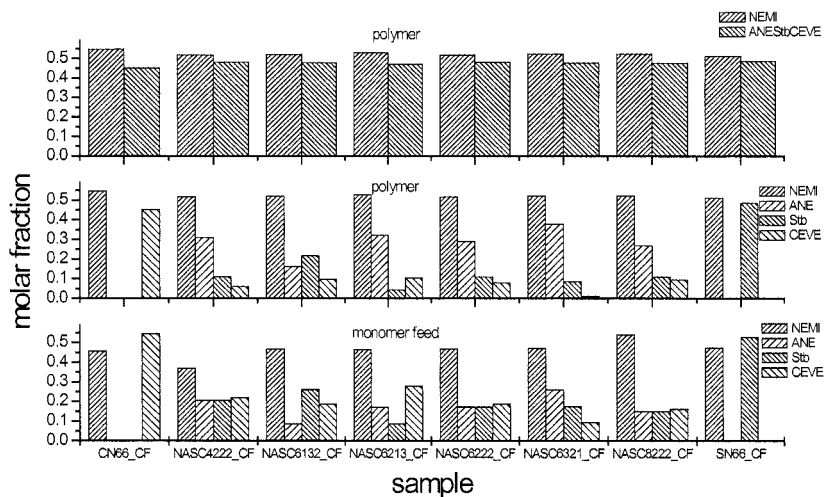


Figure 5. Quaterpolymerization diagram of the system NEMI/ANE/Stb/CEVE in chloroform at 60°C with AIBN as initiator

Similarly as in the system MSA/ANE/Stb/CEVE ANE is more incorporated into the

polymers than the other two donor monomers Stb and CEVE. On the other hand, all polymers contain more than 50 mol-% NEMI, due to the homopolymerizability of NEMI. Here a chain sequence NEMI-NEMI is possible.

3. Relative reactivities

According to the free monomer model the relative reactivities of the three donor monomers against the common acceptor macroradical in the system NEMI/ANE/Stb/CEVE can be determined (eq. 1). For this purpose the molar ratios of Stb or CEVE in the polymers and in the monomer feeds are plotted against the same ratio of ANE (Figure 6 and Figure 7).

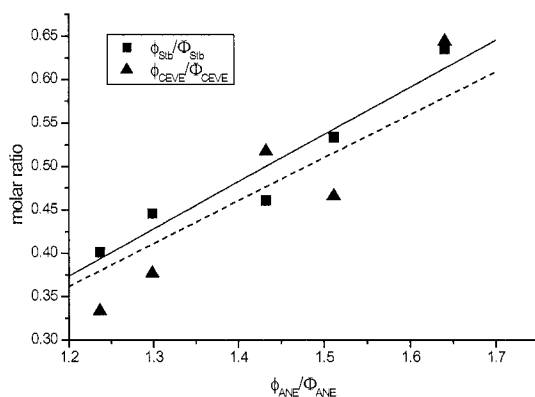


Figure 6. Determination of the relative reactivity of the three donor-monomers in the system NEMI/ANE/Stb/CEVE in THF at 60°C

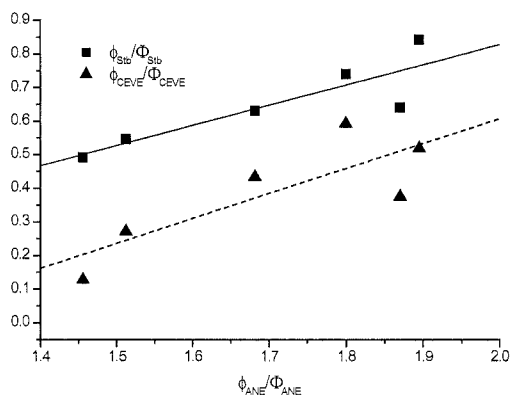


Figure 7. Determination of the relative reactivity of the three donor-monomers in the system NEMI/ANE/Stb/CEVE in chloroform at 60°C

The slope of the fitting straight lines give the relative reactivities of ANE (M_2), Stb (M_3) and CEVE (M_4) against the common radical $\sim NEMI \cdot$ ($\sim M_1 \cdot$). The results

show $k_{12} : k_{13} : k_{14} = 1.00 : 0.54 : 0.49$ for tetrahydrofuran as solvent and $k_{12} : k_{13} : k_{14} = 1.00 : 0.60 : 0.74$ for chloroform as solvent. In both solvents ANE has the highest reactivity. In tetrahydrofuran Stb is a little more reactive than CEVE and in chloroform CEVE is more reactive than Stb.

The comparison of the compositions of the polymers and the monomer feeds gives the following results for the system MSA/ANE/Stb/CEVE:

$k_{12} : k_{13} : k_{14} = 1.00 : 0.26 : 0.38$ in tetrahydrofuran

$k_{12} : k_{13} : k_{14} = 1.00 : 0.09 : 0.05$ in chloroform

Here ANE has also the highest reactivity of the three donor monomers. The reactivity ratios between Stb and CEVE in chloroform show a reverse order as in tetrahydrofuran.

Comparing the system MSA/ANE/Stb/CEVE and NEMI/ANE/Stb/CEVE demonstrates the different reactivity ratios of the three donor monomers.

Obviously, the reactivities of the donor monomers are influenced by the common acceptor monomer and by the solvents. Therefore, the results from one system cannot be transferred to other systems.

Conclusions

The monomers maleic anhydride, fumaronitrile, N-ethylmaleimide, trans-anethole, vinyl-iso-butylether, trans-stilbene and 2-chloroethyl vinyl ether were not homopolymerizable except N-ethylmaleimide. Their quaterpolymerizations give polymers with always about 50 mol-% acceptor- and 50 mol-% donor-monomer units. Due to the chain transfer to the solvents tetrahydrofuran and chloroform the polymers have rather low molecular weights. Because of the acceptor or donor character of the monomers and the used solvents the monomer reactivities are dependent on the special system and solvent. The here first described quaterpolymerization diagram is able to illustrate the copolymerization with more than three monomers.

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