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Polymers from Non-Homopolymerizable Monomers

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SUMMARY: There are many inorganic and organic compounds known which are not able to homopolymerize either with well-known polymerizable monomers or even with other non-homopolymerizable compounds. The participation of non-homopolymerizable comonomers with reactivity ratios close to 0 results in copolymers with more or less alternating structure, whereas for a strictly alternating copolymer, both reactivity ratios must be 0. Binary copolymerizations of non-homopolymerizable and homopolymerizable monomers can give information on the topochemistry, and also on the kinetics of such processes, as in these cases the number of propagating steps is remarkably reduced.

Up to now, very little is known on the terpolymerization of three non-homopolymerizable comonomers. Experimental investigations have shown that only combinations of two monomers with electron donor and one monomer with electron acceptor properties or vice versa yield terpolymers, whereas from three monomers of similar electronic behavior, no terpolymers are obtained. All such terpolymers are of alternating structure where a donor unit is succeeded by an acceptor unit.

For copolymerizations of two or three non-homopolymerizable monomers, two different mechanisms must be considered: the so-called complex model postulates the incorporation of donor-acceptor complexes of the monomers into the growing chain, whereas with the terminal or penultimate model the addition of free monomers to growing macroradicals is described. Measurements of the rate of polymerization in combination with determinations of the complex constants of the involved donor and acceptor monomer pairs together with a new kinetic scheme allow us to distinguish between the simultaneous participation of free monomers and complexes in the polymerization process.

Introduction

Besides the countless number of monomers which can undergo free radical homopolymerization there is also known a large variety of inorganic and organic compounds which are not able to homopolymerize but can form copolymers either with well polymerizable monomers or even with other non-homopolymerizable compounds. The copolymerization of binary and ternary systems with participation of non-homopolymerizable

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2. A large number of experimental investigations shows that two electron donors or two electron acceptors cannot form copolymers. But it is also well known that a powerful electron acceptor and a powerful electron donor can undergo a spontaneous copolymerization even in the absence of any initiator at rather low temperatures producing polymers with alternating structures.
3. The Q,e-scheme of Alfrey and Price can be used to visualize the behaviour of non-homopolymerizable monomers (Fig. 1). Even if this scheme provides only a qualitative guide to the copolymerization behaviour of non-homopolymerizable monomers it can be used to classify such systems. Experimental results show that for pairs of non-homopolymerizable comonomers the Q,e-values must be of opposite sign and should show a difference of at least one or two e-units to be able to form copolymers. A special problem are α-olefines with low resonance stabilization and small polarity which limits not only their free radical homopolymerization but also the copolymerization with a large number of interesting comonomers. Their values of Q are very close to 0 and the e-values are in the order of –0,2 to –0,3. They are therefore not included in Fig. 1.

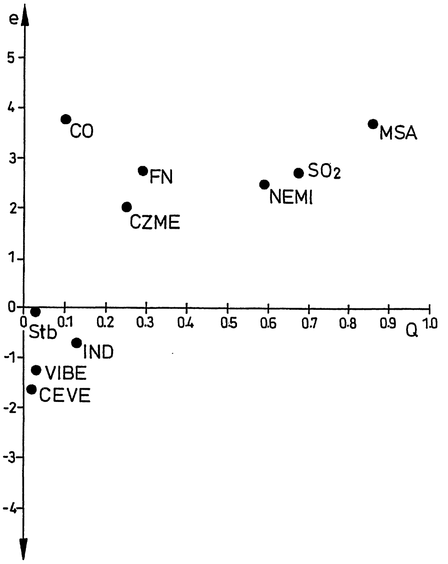


Fig. 1. Q, e-map of some non-homopolymerizable monomers. CO: carbon monoxide; FN: fumaro dinitril; MSA: maleic acid anhydride; SO_2: sulfur dioxide; NEMI: N-ethyl maleic anhydride; CZME: methyl α-cyanocinnamate; StB: trans-stilbene; IND: indene; VIBE: vinyl-isobutyl ether; CEVE: chloroethyl(vinyl)ether.

monomers is of high scientific interest as it offers information on the reactivity of such compounds against free radicals and growing macroradicals but also on the topochemistry of radical addition reactions. But there is also practical interest as some non-homopolymerizable compounds can be used for the preparation of new polymers. This may be of technical importance as in the last two decades only very few new polymerizable monomers became available.

Table 1 shows some examples of inorganic and organic monomers which were not able to homopolymerize. Among those substituted α-olefines may be of special interest. They can be devided in electron-rich donators and electron attracting acceptors.

Table 1. Non-homopolymerizable monomers

Inorganic Monomers:
- CO, SO_2, O_2

Organic Monomers:
- Phosphines
- Cyclic Disulfides
- Nitroso Compounds
- Quinones
- Olefines:
  - Elektron donors:
    - higher α-olefines $CH_2{=}CH{-}(CH_2)_n{-}X$
    - Indene
    - Anethole
    - Vinyl ethers
    - trans-Stilbene
  - Elektron acceptors:
    - Maleic acid anhydride
    - N-Alkyl maleic amides
    - Fumaric esters, dinitril
    - α-Cyano cinnamic acid esters

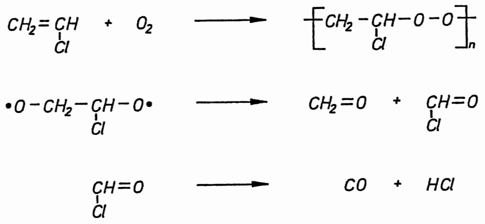
Up to now there is no theoretical classification or definition of the term "non-homopolymerizable" available but there are some empirical results which can be used to describe the behaviour of compounds which cannot homopolymerize:

1. The rate constant of homopolymerization k_{11} is about 0. Therefore the product of the reactivity ratios of the binary copolymerization with such substances ($r_1 \cdot r_2$) is also very close to 0.

Binary copolymers with non-homopolymerizable monomers

There are two possibilities for binary systems with participation of non-homopolymerizable comonomers. In case of a combination of a homopolymerizable with a non-homopolymerizable monomer the latter is incorporated as isolated units in the growing polymer chain, whereas the homopolymerizable monomer can form more or less long sequences between the units from the non-homopolymerizable monomer. Depending from the reactivity ratio and the monomer feed the homopolymerizable monomer is incorporated at least to 50 mole-% or in many cases to much more. In systems where both comonomers are not homopolymerizable the resulting copolymers contain equal molar concentrations of the two monomers and the copolymer shows a strong alternating structure.

As an interesting example for the copolymerization between a homopolymerizable and a non-homopolymerizable comonomer the polymerization of vinyl chloride in presence of molecular oxygen may be discussed. In this and a large number of similar cases first polymeric peroxides are formed which are unstable under the polymerization conditions. By decomposition of the polymeric vinyl chloride peroxides besides formaldehyde formyl chloride is formed which is unstable and yields carbon monoxide and hydrogen chloride[1].



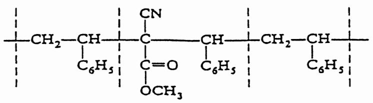
$$CH_2{=}\underset{Cl}{\underset{|}{CH}} + O_2 \longrightarrow \left[CH_2-\underset{Cl}{\underset{|}{CH}}-O-O \right]_n$$

$$\bullet O-CH_2-\underset{Cl}{\underset{|}{CH}}-O\bullet \longrightarrow CH_2{=}O + \underset{Cl}{\underset{|}{CH}}{=}O$$

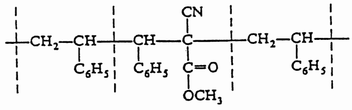
$$\underset{Cl}{\underset{|}{CH}}{=}O \longrightarrow CO + HCl$$

As carbon monoxide is also a non-homopolymerizable but copolymerizable comonomer it is incorporated in the further course of the vinylchloride polymerization resulting in carbonyl groups in the polymer chains. As these carbonyl groups are possible initiating sites of the dehydrochlorination of poly(vinyl chloride) polymers which are formed in presence of oxygen can show an increased rate of dehydrochlorination compared to PVC which is obtained under complete exclusion of oxygen[2].

Another pair of a homopolymerizable and a non-homopolymerizable comonomer can be used to discuss the topochemistry of the growing polymer chain. In case of the copolymerization of styrene and methyl α-cyanocinnamate two kinds of addition of the non-homopolymerizable ester on the growing styrene end unit are possible. These additions can be considered as head-to-head or head-to-tail structures.



head to head



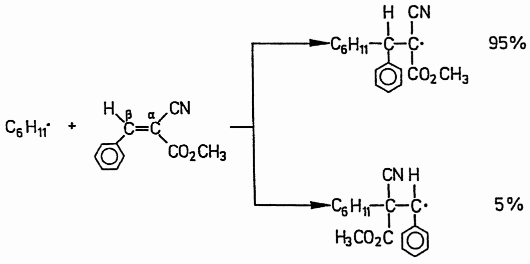
head to tail

Investigations of the addition of alkyl radicals from alkyl mercury chloride and sodium boro tetrahydride have shown that about 95% of the addition occurs with formation of the expected higher stabilized radical with two α-substituents, whereas the opposite addition occurs only to about 5%[3].

$$C_6H_{11}HgCl \xrightarrow{NaBH_4} C_6H_{11}HgH \longrightarrow C_6H_{11}\cdot$$

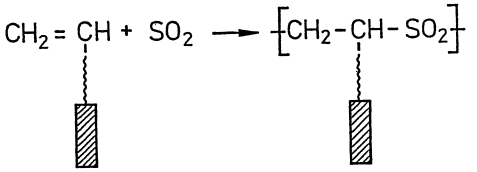
$$C_6H_{11}\cdot + \text{Alken} \longrightarrow C_6H_{11}\text{-Alkan}\cdot$$

$$C_6H_{11}\text{-Alkan}\cdot \xrightarrow{C_6H_{11}HgH} C_6H_{11}\text{-Alkan-H}$$



This may be the reason why the free radical copolymerization of these two monomers can be better described by the penultimate model instead of the terminal model[4]. But of course this finding does not answer the question whether there is a true penultimate effect or only a difference in the reactivity of the two possible ester end groups of the growing chain.

As an example for the copolymerization of two non-homopolymerizable monomers the formation of liquid crystalline polysulfones may be discussed[5, 6]. As is well known the liquid crystalline state of polymers requires sufficient mobility of the mesogenic units. In case of liquid crystalline side chain polymers this is realized by incorporating a spacer between the polymerizable group and the mesogenic unit. From the experimental point of view it would be very easy to prepare such monomers from α-olefines with a functional group, e.g. a carboxylic group in the ω-position. But due to the mentioned difficulties in free radical polymerization of α-olefines it is not possible to homopolymerize such mesogenic α-olefines. But it is possible to use the copolymerizability of α-olefines with sulfur dioxide to obtain liquid crystal polymers.



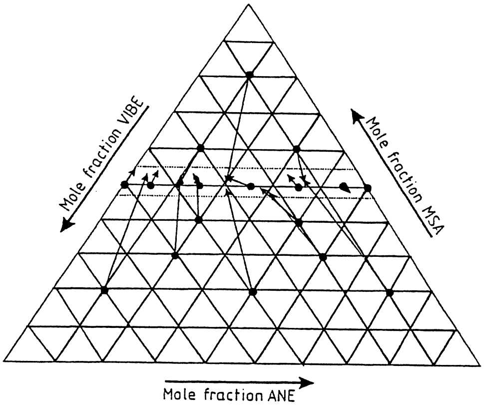
$$CH_2=CH + SO_2 \longrightarrow \left[CH_2-CH-SO_2 \right]$$

Such poly(olefinsulfones) are cleaved under the influence of ionisation radiation, e.g. by β-rays. This decomposition can be used for image forming processes[7].

Three non-homopolymerizable monomers

Whereas a lot of information is available on binary copolymerizations with participation of non-homopolymerizable comonomers only very little is known about such ternary systems. Depending on the combination of three homopolymerizable and non-homopolymerizable comonomers twelve different systems are possible. The following discussion is confined on terpolymerizations with three non-homopolymerizable comonomers. Similar as in the case of binary systems also ternary copolymers were only obtained by combination of one or two electron donors and one or two electron acceptor monomers. For such copolymerizations two different mechanisms must be considered: The so-called complex model postulates the incorporation of donor-acceptor-complexes of the monomers into the growing chain whereas by the terminal or penultimate model the addition of free monomers on the growing macroradicals is described.

The relation between monomer feed and copolymer composition can be described by Slowcombe-diagrams (Fig. 2). In all cases independent whether two acceptor monomers are combined with one donor or vice versa the overall composition is given by 50 mole-% units from donor and 50 mole-% from acceptor monomer units. As this is only possible by an alternating structure, such terpolymers can also be considered as alternating copolymers. In all systems which were analysed up to now it could be shown that real terpolymers are obtained and in no case mixtures of two binary copolymers from acceptor and donor pairs$^{8)}$.



o— = Feed composition
→ = Terpolymer composition

Fig. 2. Slocombe diagram of the terpolymerization of N-ethyl maleimide (NEMI),methyl α-cyanocinnamate (CZME) and indene (IND).

As an example, the terpolymerization of one acceptor monomer (maleic anhydride) with two donor monomers (vinyl-iso-butylether and anethole) may be discussed, where all terpolymers contain 50 mole-% maleic anhydride units. The mole-fraction of the two donor monomers in the terpolymers depends on the composition of the monomer feed. In all cases vinyl-iso-butylether is more reactive than anethol; from determination of the composition the reactivity ratio of the two free donor monomers is about two. If one considers the polymerization as a "copolymerization" of two complexes between the acceptor and the two donor molecules about the same reactivity ratio is obtained$^{8)}$. This shows that the overall composition of the copolymers does not allow a decision on the respective reaction mechanism. This is only possible if one determines the rate of the terpolymerization and the complex forming constants.

The kinetic scheme of the chain growth with participation of free monomers and the possible charge-transfer complexes can be combined to the overall reaction rate with free (f) and complexed (CT) monomers[9)]:

$$v_{br} = v_p(f) + v_p(CT)$$

Measuring the complex constants, the overall composition of the terpolymers and the rate of polymerization in dependence on the electron-acceptor monomer concentration allows to determine the participation of all monomer species in the chain growth process. In the case of N-ethyl-maleinimide, anethole and stilbene can be shown that the participation of free monomers is rather independent from the acceptor concentration whereas the participation of complexes increases with the acceptor concentration which means that also the concentration of complexes increases[10)] (Fig. 3). This is the first time where for the case of terpolymerizations of three non-homopolymerizable monomers could be shown that free monomers and complexes participate simultaneously in the propagating process.

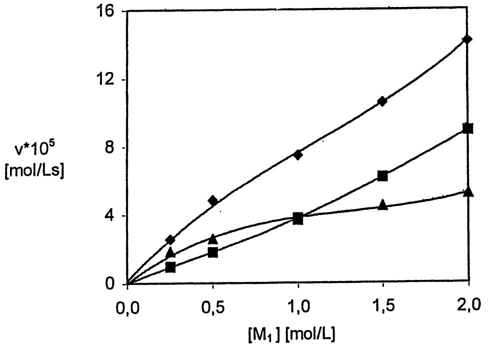


Fig. 3. Rate of terpolymerization of N-ethyl maleimide (M_1), anethole (M_2) and stilbene (M_3) in dependence on [M_1].

(◆) v_{Br}; (■) $v_p(CT)$; (▲) $v_p(f)$: (CCl_4, 60°C, $2 \cdot 10^{-4}$ mol·L^{-1} A. [M_2]=[M_3]= 0,25 mol L^{-1}).

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