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Solvent Effect on Free-Radical Chain Polymerization. 7.[†] Kinetical Analysis of the Binary System Methyl Methacrylate/*N*-Vinylpyrrolidone in Bulk and in Model Solvents in Terms of the Reactant–Solvent Complex Model

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ABSTRACT: The monomer system methyl methacrylate (MMA = M_1)/*N*-vinylpyrrolidone (NVP = M_2) was copolymerized at 60 °C with azobis(isobutyronitrile) as the initiator in cyclohexane (c-H), methyl isobutyrate (MiB), and *N*-methylpyrrolidone (NMP) at the total monomer concentration 0.4 (mol·L^{-1}). The relative reactivity ratios r_i were estimated by the nonlinear least-squares curve fitting by Tidwell and Mortimer, and they depend on the nature of the solvent. For the description of this effect the reactant–solvent complex (RSC) model was taken into consideration. Since the analytical copolymer composition equation derived is inconvenient for very small r_i values, the Monte Carlo method was used. It permits us to describe all tendencies correctly in terms of the RSC model. In the present paper the RSC model was tested for the first time in application to a binary copolymerization, whereby preevaluated relative reactivity parameters were used instead of fitting the model to experimental data. In this manner a check of the physical meaning of the model increments was achieved. The highest deviation between measured and calculated copolymer compositions amounted to 3–5 mol %. Solvents especially affect the resonance parameter Q of the monomers which changes 4-fold by a change from c-H to NMP. The polarity parameter e remains almost unchanged. Observed effects can be understood in terms of the molecular orbital (MO) energies of the reacting partners.

1. Introduction

Particular attention was paid in the 1980s to the understanding of the reaction mechanism of binary alternating systems.[1–5] Since Lewis acid–base (EDA) interactions between the monomers were frequently found in such systems, the significance of the monomer–monomer complexation for reaction kinetics was extensively discussed. In the complex models proposed an equilibrium of the complex formation was postulated. As a result both free monomers can add separately or monomers bound in complex add in pairs to the growing radical. Even polymerization of complexes as independent kinetical species, known as complexomers, was taken into account.[2] The models proposed contain some important simplifications such as no complexation of radicals and no reactivity changes of monomers complexed by solvents. Solvents were, however, assumed to affect the monomer–monomer complexation by shifting the complex equilibrium with dilution. In this regard not only monomer–monomer but monomer–solvent complex equilibrium constants K were estimated.[6–8] By means of these measurements a quantitative treatment of complex models was the object of discussions.

In some cases, however, little or no solvent effects on copolymerization kinetics were found in spite of an evident presence of complexes between monomers.[9–11] It was proposed in this connection that monomers add separately to the growing macroradical, with pronounced significance of the cross propagation expressed by the constant ratio k_{p12}/k_{p21}.[12–14] All the main effects typical for an alternating copolymerization such as rate maximum and its shift with solvent change and/or increasing dilution were explained without taking into account any complex formation between monomers. The above-mentioned ratio of cross-propagation constants depends, however, on the reaction medium, which was not discussed in detail. A careful discussion of the solvent effect on propagation rate constants, as summarized in ref 5, could contribute to a more efficient modeling of the solvent effect on the copolymer composition and on the copolymerization rate.

The aim of the present work is to adopt the reactant–solvent complex (RSC) model introduced for the homopolymerization kinetics in refs 15 and 16 for binary copolymerization modeling. It was applied for the description of the solvent dependence of copolymer composition on solvents of the system methyl methacrylate (MMA = M_1)/*N*-vinylpyrrolidone (NVP = M_2). Polymerizations in bulk and in cyclohexane (c-H) and in two model solvents methyl isobutyrate (MiB) and *N*-methylpyrrolidone (NMP) are considered at high dilution.

2. Theoretical Part

As was discussed in ref 17, in the condensed phase monomer and radical molecules are in fact still (even in bulk) influenced by neighboring molecules by Lewis acid–base (EDA), polar, or dispersive interactions. As result energies of molecular orbitals, i.e., the reactivities of the substrates, are affected in this way. It seems unlikely to operate without taking into account any radical (monomer)-medium interaction, on the one hand, and, on the other, it is convincingly shown that complexed and uncomplexed monomers can add to complexed and uncomplexed radicals, supposing that complexations are unspecific equilibrium processes. As can be seen, both points of view presented in the Introduction may be simultaneously valid; i.e., they do not exclude each other.

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Both ideas are unified by means of the RSC model. For the usage of this model the following assumptions were made:

1. Pure monomers do not affect their own reactivity (intraactions are kinetically inefficient); a model solvent very similar to the monomer does not affect the monomer reactivity either as related to the bulk state.
2. Only equilibrium 1:1 complexes are considered.
3. The relative reactivity ratios are estimated in systems which are diluted "highly enough" in the respective solvents.

The following abbreviations are applied ($\overline{\mathrm{AB}}$ = complex of molecules A and B; important! the succession AB suggests that A will react as influenced by B):

in bulk	in solvent S (high dilution)	symbol
M_1	M_1	M_1
M_2	M_2	M_2
$\overline{\mathrm{M}_1\mathrm{M}_2}$	$\overline{\mathrm{M}_1\mathrm{S}_2}$	M_3
$\overline{\mathrm{M}_2\mathrm{M}_1}$	$\overline{\mathrm{M}_2\mathrm{S}_1}$	M_4
$\sim\mathrm{M}_1^{\bullet}$	$\sim\mathrm{M}_1^{\bullet}$	$\sim\mathrm{M}_1^{\bullet}$
$\sim\mathrm{M}_2^{\bullet}$	$\sim\mathrm{M}_2^{\bullet}$	$\sim\mathrm{M}_2^{\bullet}$
$\sim\overline{\mathrm{M}_1^{\bullet}\mathrm{M}_2}$	$\sim\overline{\mathrm{M}_1^{\bullet}\mathrm{S}_2}$	$\sim\mathrm{M}_3^{\bullet}$
$\sim\overline{\mathrm{M}_2^{\bullet}\mathrm{M}_1}$	$\sim\overline{\mathrm{M}_2^{\bullet}\mathrm{S}_1}$	$\sim\mathrm{M}_4^{\bullet}$

The following is further assumed for complex equilibrium constants K (M_i = monomer, S_i = solvent):

for $\overline{\mathrm{M}_1\mathrm{M}_2}$ equilibrium: K

for $\overline{\mathrm{M}_1\mathrm{S}_2}$ equilibrium: $K_1 = K$, when S_2 is a model of M_2

for $\overline{\mathrm{M}_2\mathrm{S}_1}$ equilibrium: $K_2 = K$, when S_1 is a model of M_1

Using the abbreviations k = rate constant, R = reaction rate, I = initiator, f = initiator efficiency factor, and p = polymer and indices ini = initiation, d = dissociation, p = propagation, and t = chain termination, the reaction scheme of the RSC model applied to a binary copolymerization takes the shape of a quaternary copolymerization:

Initiation

$$\mathrm{I} \rightarrow 2\mathrm{R}^{\bullet} \qquad R_{\mathrm{ini}} = 2k_{\mathrm{d}}f[\mathrm{I}] \tag{1}$$

$$\mathrm{R}^{\bullet} + \mathrm{M}_i \rightarrow {\sim}\mathrm{M}_i^{\bullet} \qquad i = 1, 2, 3, \text{ or } 4 \tag{2}$$

Propagation

$${\sim}\mathrm{M}_i^{\bullet} + \mathrm{M}_j \xrightarrow{k_{\mathrm{p}ij}} {\sim}\mathrm{M}_j^{\bullet} \qquad R_{\mathrm{p}ij} = k_{\mathrm{p}ij}\,[{\sim}\mathrm{M}_i^{\bullet}][\mathrm{M}_j] \tag{3}$$

with $i = 1-4$ and $j = 1-4$. From all $i-j$ combinations 16 propagation steps result.

Termination

$${\sim}\mathrm{M}_i^{\bullet} + {}^{\bullet}\mathrm{M}_j{\sim} \xrightarrow{k_{\mathrm{t}ij}} \mathrm{P} \qquad R_{\mathrm{t}ij} = k_{\mathrm{t}ij}\,[{\sim}\mathrm{M}_i^{\bullet}]\,[{\sim}\mathrm{M}_j^{\bullet}] \tag{4}$$

with $i = 1-4$ and $j = 1-4$. From all $i-j$ combinations 10 different termination steps result.

Table 1. Relative Reactivity Ratios r_{ij}, Their General Meaning According to the Conventional Quaternary Model, the Meaning in the Sense of the RSC Model, and Their Numerical Values

reaction ratio	quaternary model	RSC model	value (TM estimation)
		Heteropropagation	
r_{12}	$k_{\mathrm{p}11}/k_{\mathrm{p}12}$	$k_{\mathrm{p}1\,1}/k_{\mathrm{p}1\,2}$	2.073
r_{21}	$k_{\mathrm{p}22}/k_{\mathrm{p}21}$	$k_{\mathrm{p}2\,2}/k_{\mathrm{p}2\,1}$	0.027
r_{23}	$k_{\mathrm{p}22}/k_{\mathrm{p}23}$	$k_{\mathrm{p}2\,2}/k_{\mathrm{p}2\,\overline{12}}$	0.014
r_{32}	$k_{\mathrm{p}33}/k_{\mathrm{p}32}$	$k_{\mathrm{p}\overline{21}\,\overline{12}}/k_{\mathrm{p}\overline{21}\,2}$	5.932
r_{34}	$k_{\mathrm{p}33}/k_{\mathrm{p}34}$	$k_{\mathrm{p}\overline{21}\,\overline{12}}/k_{\mathrm{p}\overline{21}\,\overline{21}}$	13.68
r_{43}	$k_{\mathrm{p}44}/k_{\mathrm{p}43}$	$k_{\mathrm{p}\overline{12}\,\overline{21}}/k_{\mathrm{p}\overline{12}\,\overline{12}}$	0.003
r_{14}	$k_{\mathrm{p}11}/k_{\mathrm{p}14}$	$k_{\mathrm{p}1\,1}/k_{\mathrm{p}1\,\overline{21}}$	4.781
r_{41}	$k_{\mathrm{p}44}/k_{\mathrm{p}41}$	$k_{\mathrm{p}\overline{12}\,\overline{21}}/k_{\mathrm{p}\overline{12}\,1}$	0.006
		Homopropagation	
r_{13}	$k_{\mathrm{p}11}/k_{\mathrm{p}13}$	$k_{\mathrm{p}1\,1}/k_{\mathrm{p}1\,\overline{12}}$	0.592
r_{31}	$k_{\mathrm{p}33}/k_{\mathrm{p}31}$	$k_{\mathrm{p}\overline{21}\,\overline{12}}/k_{\mathrm{p}\overline{21}\,1}$	1.779
r_{24}	$k_{\mathrm{p}22}/k_{\mathrm{p}24}$	$k_{\mathrm{p}2\,2}/k_{\mathrm{p}2\,\overline{21}}$	1.638
r_{42}	$k_{\mathrm{p}44}/k_{\mathrm{p}42}$	$k_{\mathrm{p}\overline{12}\,\overline{21}}/k_{\mathrm{p}\overline{12}\,2}$	0.610

It follows generally that:

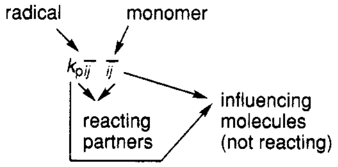
number of reactands: $n = 4$

number of propagation steps: $n^2 = 16$

number of relative reactivity ratios:

$$n^2 - n = 2\binom{n}{n-2} = 12$$

Table 1 contains the relative reactivity ratios r_{ij}, their conventional meaning (quaternary model), and their meaning in the sense of the RSC model. The following code of indices was used for the RSC model:



For determination of the r_{ij} values according to the RSC model, it was assumed that the r_{ij} values obtained by means of the classical (two-parameter) model in different solvents keep a physical meaning even if they vary from solvent to solvent. In other words, it was supposed that the r_{ij} values yield appropriate information about the solvent effect on the relative reactivity of monomers. Consequently, the experimental r_{ij} values should be linked as follows:

1. During copolymerization in an inert solvent, no interaction takes place; r_{ij} values correspond to r_{12} and r_{21} in Table 1.
2. In a solvent S being very similar to M_2 (model solvent S_2, e.g., a saturated derivative of M_2), M_1 is practically fully complexed by $\mathrm{S}_2 + \mathrm{M}_2$; r_{ij} values obtained under this condition correspond to r_{23} and r_{32}.
3. In S_1 as a model of M_1, M_2 is totally complexed by $\mathrm{S}_1 + \mathrm{M}_1$; here r_{ij} values are linked to r_{14} and r_{41}.
4. Since the system $\mathrm{M}_1/\mathrm{M}_2$ cannot be investigated at the same time in S_1 and S_2, both in excess, r_{34} and r_{43}

can only be estimated indirectly. In the present work the following approximations were used:

$$r_{34} = r_{14}r_{32}/r_{12}$$

$$r_{43} = r_{23}r_{41}/r_{21}$$

Other possibilities are:

$$r_{34} = r_{14}/r_{13} \quad \text{or} \quad r_{32}r_{24}$$

$$r_{43} = r_{23}/r_{24} \quad \text{or} \quad r_{41}r_{13}$$

All of them require the assumption that the uncomplexed and complexed radicals have the same reactivity.

5. r_{13} and r_{31} can be estimated from homopolymerization rate measurements of M_1 in S_2 as solvent.[15,16]

6. In analogy to point 5 ratios r_{24} and r_{42} were calculated from homopolymerization rate measurements of M_2 in S_1 as solvent. 10 of the 12 reactivity ratios contained in Table 1 are directly accessible, which makes the RSC model worth examining.

(a) Analytical Copolymerization Equation. In the case of a stationary polymerization it is assumed that the production rate of each sort of radical is equal to the consumption rate. According to Walling and Briggs:[18]

$$R_{\mathrm{p12}} + R_{\mathrm{p13}} + R_{\mathrm{p14}} = R_{\mathrm{p21}} + R_{\mathrm{p31}} + R_{\mathrm{p41}} \tag{5}$$

$$R_{\mathrm{p21}} + R_{\mathrm{p23}} + R_{\mathrm{p24}} = R_{\mathrm{p12}} + R_{\mathrm{p32}} + R_{\mathrm{p42}} \tag{6}$$

$$R_{\mathrm{p32}} + R_{\mathrm{p32}} + R_{\mathrm{p34}} = R_{\mathrm{p13}} + R_{\mathrm{p23}} + R_{\mathrm{p43}} \tag{7}$$

$$R_{\mathrm{p41}} + R_{\mathrm{p42}} + R_{\mathrm{p43}} = R_{\mathrm{p14}} + R_{\mathrm{p24}} + R_{\mathrm{p34}} \tag{8}$$

It follows from ref 18 that:

$$k_{\mathrm{p11}}[\sim M_1^{\bullet}] = \Delta_1 \tag{9}$$

$$k_{\mathrm{p22}}[\sim M_2^{\bullet}] = \Delta_2 \tag{10}$$

$$k_{\mathrm{p33}}[\sim M_3^{\bullet}] = \Delta_3 \tag{11}$$

$$k_{\mathrm{p44}}[\sim M_4^{\bullet}] = \Delta_4 \tag{12}$$

with

$$\Delta_1 = \begin{bmatrix} \frac{[M_1]}{r_{21}} & \frac{[M_1]}{r_{31}} & \frac{[M_1]}{r_{41}} \\ -\left(\frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}} + \frac{[M_4]}{r_{24}}\right) & \frac{[M_2]}{r_{32}} & \frac{[M_2]}{r_{42}} \\ \frac{[M_3]}{r_{23}} & -\left(\frac{[M_1]}{r_{31}} + \frac{[M_2]}{r_{32}} + \frac{[M_4]}{r_{34}}\right) & \frac{[M_3]}{r_{43}} \end{bmatrix} \tag{13}$$

$$\Delta_2 = \begin{bmatrix} -\left(\frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}} + \frac{[M_4]}{r_{14}}\right) & \frac{[M_1]}{r_{31}} & \frac{[M_1]}{r_{41}} \\ \frac{[M_2]}{r_{21}} & \frac{[M_2]}{r_{32}} & \frac{[M_2]}{r_{42}} \\ \frac{[M_3]}{r_{13}} & -\left(\frac{[M_1]}{r_{31}} + \frac{[M_2]}{r_{32}} + \frac{[M_4]}{r_{34}}\right) & \frac{[M_3]}{r_{43}} \end{bmatrix} \tag{14}$$

$$\Delta_3 = \begin{bmatrix} -\left(\frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}} + \frac{[M_4]}{r_{14}}\right) & \frac{[M_1]}{r_{31}} & \frac{[M_1]}{r_{41}} \\ \frac{[M_2]}{r_{12}} & -\left(\frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}} + \frac{[M_4]}{r_{24}}\right) & \frac{[M_2]}{r_{42}} \\ \frac{[M_3]}{r_{13}} & \frac{[M_3]}{r_{23}} & \frac{[M_3]}{r_{43}} \end{bmatrix} \tag{15}$$

$$\Delta_4 = \begin{bmatrix} -\left(\frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}} + \frac{[M_4]}{r_{14}}\right) & \frac{[M_1]}{r_{21}} & \frac{[M_1]}{r_{31}} \\ \frac{[M_2]}{r_{12}} & -\left(\frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}} + \frac{[M_4]}{r_{24}}\right) & \frac{[M_2]}{r_{32}} \\ \frac{[M_3]}{r_{13}} & \frac{[M_3]}{r_{23}} & -\left(\frac{[M_1]}{r_{31}} + \frac{[M_2]}{r_{32}} + \frac{[M_4]}{r_{34}}\right) \end{bmatrix} \tag{16}$$

For monomer consumption in the initial stages of the polymerization, one obtains:

$$-\mathrm{d}[M_i]/\mathrm{d}t = \sum_{j=1}^{4} k_{\mathrm{p}ji}[\sim M_j^{\bullet}][M_i] \tag{17}$$

After elimination of the radical concentration by means of eqs 9–12 and introduction of the relative reactivity ratios r_{ij}, we obtain:

$$-\frac{\mathrm{d}[M_1]}{\mathrm{d}t} = [M_1]\left(\Delta_1 + \frac{\Delta_2}{r_{21}} + \frac{\Delta_3}{r_{31}} + \frac{\Delta_4}{r_{41}}\right) \tag{18}$$

$$-\frac{\mathrm{d}[M_2]}{\mathrm{d}t} = [M_2]\left(\frac{\Delta_1}{r_{12}} + \Delta_2 + \frac{\Delta_3}{r_{32}} + \frac{\Delta_4}{r_{42}}\right) \tag{19}$$

$$-\frac{\mathrm{d}[M_3]}{\mathrm{d}t} = [M_3]\left(\frac{\Delta_1}{r_{13}} + \frac{\Delta_2}{r_{23}} + \Delta_3 + \frac{\Delta_4}{r_{43}}\right) \tag{20}$$

$$-\frac{\mathrm{d}[M_4]}{\mathrm{d}t} = [M_4]\left(\frac{\Delta_1}{r_{14}} + \frac{\Delta_2}{r_{24}} + \frac{\Delta_3}{r_{34}} + \Delta_4\right) \tag{21}$$

With m_i as the mole ratio of the monomer M_i in the polymer, it follows that:

$$\frac{\mathrm{d}[M_1]}{\mathrm{d}[M_2]} = \frac{m_1}{m_2} = a$$

$$\frac{\mathrm{d}[M_2]}{\mathrm{d}[M_3]} = \frac{m_2}{m_3} = b$$

$$\frac{\mathrm{d}[M_3]}{\mathrm{d}[M_4]} = \frac{m_3}{m_4} = c \quad \text{and} \quad \sum_{i=1}^{4} m_i = 1 \tag{22}$$

Since a, b, and c are calculated first, it follows for the m_i values:

$$m_4 = 1/(1 + c + bc + abc) \tag{23}$$

$$m_3 = m_4c \tag{24}$$

$$m_2 = m_4bd \tag{25}$$

$$m_1 = m_4abc \tag{26}$$

In the copolymer no difference can be made between M_1

and M_3 monomer units and between M_2 and M_4. For comparison of the calculated polymer composition with the measured one, we can summarize:

$$m_1 \leftarrow m_1 + m_3 \quad \text{and} \quad m_2 \leftarrow m_2 + m_4$$

(b) Calculation of the Copolymer Composition by Means of the Monte Carlo Method (Markov I Statistic Chains). Another way of calculating the copolymer composition is the chain propagation simulation by means of the Monte Carlo method.[19,20] It follows from the propagation scheme (eq 3) that each radical can react with four differently reactive monomers. The probability P of each of these four reactions depends on the monomer reactivity and concentration. It is expressed for j varying from 1 to 4 as:

$$P_{ij} = \frac{R_{pij}}{R_{pi1} + R_{pi2} + R_{pi3} + R_{pi4}} \qquad (27)$$

with

$$\sum_{j=1}^{4} P_{ij} = 1 \qquad (28)$$

After substituting R_{pij} in eq 27 by eq 3 and introducing r_{ij} values, one obtains:

$$P_{ij} = \frac{\frac{1}{r_{ij}}[M_i]}{\sum_{j=1}^{4} \frac{1}{r_{ij}}[M_i]} \qquad (29)$$

with $r_{ij} = 1$ when $i = j$.

Equations 27–29 are generally valid for n components, but here they were used for $n = 4$ components. Since a stochastical character of propagation was assumed, the interval 0 to 1 was divided into four parts as follows:

1. 0 to P_{i1}
2. P_{i1} to $P_{i1} + P_{i2}$
3. $P_{i1} + P_{i2}$ to $P_{i1} + P_{i2} + P_{i3}$
4. $P_{i1} + P_{i2} + P_{i3}$ to $P_{i1} + P_{i2} + P_{i3} + P_{i4} = 1$

and a random number between 0 and 1 was drawn. Random numbers were generated by means of the program G05CAF available in a NAG (Numerical Algorithmus Group Ltd.) program collection. It has a periodicity of 10^{56}. The new monomer added to the growing chain was given the number of the part to which the random number belonged. Chains of 10^5 monomer units were generated. On this level polymer composition was reproducible with an accuracy ±0.1 mol %. Computations were carried out in analogy to ref 19.

3. Experimental Methods

Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol.

Solvents used were fractionally distilled after addition of CaH_2. The boiling points were as follows: cyclohexane, 81.5 °C at 754.5 mmHg; methyl isobutyrate, 93.2 °C at normal pressure; *N*-methylpyrrolidone, about 86 °C at 14 mmHg.

Stabilized methyl methacrylate was freed from inhibitor by washing twice with 0.2 N NaOH followed by distilled water. The monomer was dried over $CaCl_2$ and fractionally distilled under a reduced nitrogen atmosphere after addition of CaH_2. *N*-Vinylpyrrolidone was dried over $CaCl_2$ some days and fractionally bidistilled under vacuum. Its boiling point was about 96 °C at 14 mmHg.

Polymerizations were carried out in round 250-mL flasks under a N_2 atmosphere and magnetic stirring at 60 °C. A total of 150 mL of solvent and 7 mL of the total monomer mixture were used. This corresponds to the monomer mole concentration of about 0.4 (mol·L^{-1}). The initiator concentration was kept constant at 1.218×10^{-2} (mol·L^{-1}). The reaction mixture was degassed by 3-fold freeze–thawing cycles. Solvents strongly varied the reaction rate, so that conversion control was difficult. Conversion was estimated gravimetrically and varied between about 5 and 30 wt %. As precipitant, diethyl ether or petroleum ether was used. Filtered polymers were dried until they reached a constant weight. Samples assigned for compositional analyses were dissolved in chloroform and reprecipitated. The composition of the copolymers was ascertained by means of elemental and IR-spectroscopic analyses. For the last purpose, polymer films on KBr pills were recorded by means of a Perkin-Elmer instrument Type 457.

4. Results

The monomer system MMA/NVP was copolymerized in the following solvents: (1) in MiB for the specific influence of NVP, (2) in NMP for the specific influence of MMA, and (3) in cyclohexane for an uninfluenced copolymerization. Beyond these experiments results of the bulk copolymerization published in ref 21 were taken into consideration. In Tables 2–4 monomer feed used and composition of the resulting copolymers as well as reaction rates are summarized for each solvent. The composition of the copolymers was recalculated to initial conversion =0 wt % according to ref 22. Obtained mole fractions of NVP in polymers are summarized in the same tables and are plotted as a function of the NVP mole ratio in the monomer feed in Figure 1a. It can be seen that copolymer compositions measured in different solvents are not identical. Polymers synthesized in c-H still contain much more NVP than polymers obtained in other solvents and in bulk. In c-H polymerizations were heterogeneous, but there are no indications that this is primarily significant for the copolymer composition.[23] This problem will be discussed later. It is further observed that polymerizations in NMP yield products containing less NVP than polymerizations in MiB as solvent. At about 90 mol % of NVP in the feed the composition of the copolymers seems to be equal in both solvents and at more than 90 mol % NVP in the feed NVP is slightly more frequently inserted into the polymer in NMP than in MiB.

Literature results on bulk polymerization[21] are at the high MMA content very similar to the results of the polymerization in MiB.

Estimation of the Relative Reactivity Ratios. Copolymer compositions recalculated to initial conversion = 0 wt % were used for calculations of the relative reactivity ratios r_{ij} as a function of the solvent used. The calculations were carried out by means of the nonlinear least-squares curve-fitting method described by Tidwell

Table 2. Copolymerization Data of the System MMA/NVP in Methyl Isobutyrate (MiB) as Solvent ([MMA] + [NVP] = 0.4 (mol·L^{-1}), [AIBN] = 1.218 × 10^{-2} (mol·L^{-1}), 60 °C)

		m_{NVP}					
Nr	[MMA]:[NVP] mole ratio	conv = 0%	N analysis	IR analysis	t_p (s)	conv (wt %)	$R_p \times 10^6$ [a] (mol·L^{-1}·s^{-1})
MN 80	80:20	6.22	6.55	6.5	9600	12.70	5.21
MN 60	60:40	13.22	13.86	13.9	8100	10.55	5.21
MN 45	45:55	18.27	19.57	19.7	10800	13.00	4.87
MN 35	35:65	21.76	25.80	25.8	10800	14.31	5.40
MN 25	25:75	27.23	28.61	29.5	7200	7.65	4.35
MN 15	15:85	34.36	36.03	35.7	4800	6.79	5.83
MN 10	10:90	38.77	40.71	40.0	4500	6.61	6.06
MN 05	5:95	48.37	48.74	48.4	3000	4.10	5.65

[a] Calculated supposing that the volume of the reaction mixture changes by the factor 1.1 during the heating from 20 to 60 °C; one-point measurements only.

Table 3. Copolymerization Data of the System MMA/NVP in *N*-Methylpyrrolidone (NMP) as Solvent ([MMA] + [NVP] = 0.4 (mol·L^{-1}), [AIBN] = 1.218 × 10^{-2} (mol·L^{-1}), 60 °C)

		m_{NVP}					
Nr	[MMA]:[NVP] mole ratio	conv = 0%	N analysis	IR analysis	t_p (s)	conv (wt %)	$R_p \times 10^6$ [a] (mol·L^{-1}·s^{-1})
MN 80	80:20	4.02	5.25	5.7	10800	44.31	16.18
MN 60	60:40	9.62	11.88	12.9	8100	32.60	16.14
MN 45	45:55	17.44	20.77	20.4	12600	28.27	9.10
MN 35	35:65	19.61	26.18	26.4	10800	33.97	12.84
MN 25	25:75	24.85	30.52	29.5	7200	23.25	13.25
MN 15	15:85	33.55	38.53	37.7	4800	16.22	13.94
MN 10	10:90	34.33	43.68	44.6	4500	16.21	14.88
MN 05	5:95	49.93	49.93	51.5	3000	11.26	15.52

[a] See remarks in Table 2.

Table 4. Copolymerization Data of the System MMA/NVP in Cyclohexane as Solvent ([MMA] + [NVP] = 0.4 (mol·L^{-1}), [AIBN] = 1.218 × 10^{-2} (mol·L^{-1}), 60 °C)

		m_{NVP}					
Nr	[MMA]:[NVP] mole ratio	conv = 0%	N analysis	IR analysis	t_p (s)	conv (wt %)	$R_p \times 10^6$ [a] (mol·L^{-1}·s^{-1})
MN 80	80:20	14.65	14.38	14.2	20400	35.61	10.70
MN 60	60:40	21.52	22.19	22.0	8100	12.89	6.33
MN 45	45:55	26.26	27.11	27.3	9000	10.64	4.75
MN 35	35:65	30.99	32.97	33.3	9300	18.77	8.16
MN 25	25:75	39.17	40.01	41.5	8100	9.23	4.64
MN 15	15:85	46.05	46.28	47.9	2400	3.82	6.51
MN 10	10:90	48.92	49.06	48.4	3600	4.84	5.52
MN 05	5:95	58.41	57.22	57.0	3000	2.82	7.73

[a] See remarks in Table 2.

and Mortimer[24] (TM method). The following r_{ij} values were obtained:

in MiB: $r_{12} = 4.781 \pm 0.236$
$r_{21} = 0.006 \pm 2.286$

in NVP: $r_{12} = 5.932 \pm 0.198$
$r_{21} = 0.014 \pm 0.899$

in c-H: $r_{12} = 2.073 \pm 0.247$
$r_{21} = 0.027 \pm 0.0624$

in bulk: $r_{12} = 4.041 \pm 0.956$
$r_{21} = 0.066 \pm 3.965$

Modeling by Means of the Classical Model. At first, the classical copolymerization model (see the introduction in ref 24) was used to calculate the polymer composition as a function of the monomer feed composition, taking the above r_{ij} values into consideration. The obtained curves are plotted in Figure 1a. A reasonable agreement between the experimental points and calculated values can be observed except for very high NVP content in the feed. In this region the model generally predicts a much too high NVP content in the polymer.

Modeling by Means of the RSC Model. The complex equilibrium constants for systems under consideration were taken from an earlier work:[25]

for system MMA/NVP $K = 0.169 \pm 0.037$ at 30 °C

for system MiB/NVP $K = 0.112 \pm 0.024$ at 60 °C

for system MMA/NMP $K = 0.125 \pm 0.030$ at 60 °C

For evaluations in terms of the RSC model an average value of $K = 0.15$ was set.

Relative reactivity ratios r_{ij} collected in Table 1 were estimated according to the rules pointed out in the Theoretical Part. Values required for the homopropagation steps were taken from ref 16.

The knowledge of the concentration of all kinetically different monomers $[M_i]$ is further needed for calculations. The simulation of the solvent effect was carried out as follows:

1. In c-H and in bulk the concentration of the complex $\overline{M_1M_2}$ was directly calculated from $[M_1]_0$ and $[M_2]_0$ (concentrations of uncomplexed monomers);[15] one obtains respectively:

$$[M_1] = [M_1]_0 - [\overline{M_1M_2}]$$

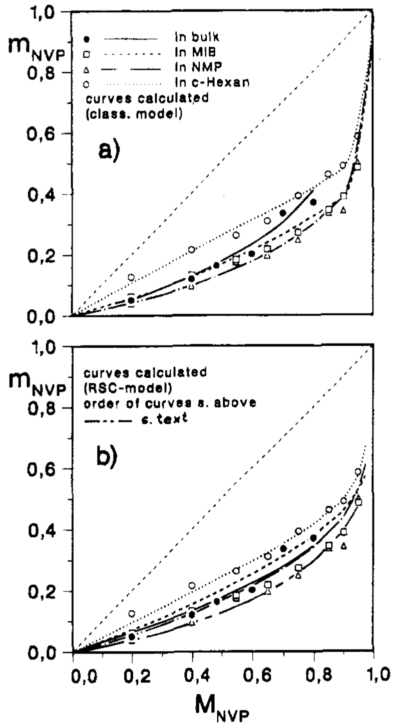


Figure 1. Copolymerization diagram for the system MMA/NVP measured in different solvents at 60 °C with AIBN as initiator, $[M_1] + [M_2] \approx 0.4$ (mol·L^{-1}): (a) measured points; curves calculated by means of the classical two-parameter model; (b) calculated by means of the reactant–solvent complex model (for the set of constants, see Table 1).

$$[M_2] = [M_2]_0 - [\overline{M_1M_2}]$$

$$[M_3] = [\overline{M_1M_2}]$$

$$[M_4] = [\overline{M_2M_1}]$$

2. In MiB (=S_1) the concentration of the complex between NVP and the sum of MMA and MiB was calculated;[15] i.e.:

$$[\text{complex}] = [\overline{M_2M_1}] + [\overline{M_2S_1}]$$

Since concentrations on the right side of the above equation are not known, it was assumed that:

$$[\overline{M_2M_1}] = [\text{complex}]\frac{[M_1]_0}{[M_1]_0 + [S_1]_0}$$

It was further set that:

$$[M_1] = [M_1]_0 - [\overline{M_2M_1}]$$

$$[M_2] = [M_2]_0 - [\text{complex}]$$

$$[M_3] = [\overline{M_1M_2}]$$

$$[M_4] = [\text{complex}]$$

3. In NMP (=S_2) the concentration of the complex between MMA and the sum of NVP and NMP was similarly computed.[15] In analogy to method 2 it follows that:

$$[\text{complex}] = [\overline{M_1M_2}] + [\overline{M_1S_2}]$$

whereby concentrations on the right side of this equation are not known. It was assumed as well that:

$$[\overline{M_1M_2}] = [\text{complex}]\frac{[M_2]_0}{[M_2]_0 + [S_2]_0}$$

and

$$[M_1] = [M_1]_0 - [\text{complex}]$$

$$[M_2] = [M_2]_0 - [\overline{M_1M_2}]$$

$$[M_3] = [\text{complex}]$$

$$[M_4] = [\overline{M_1M_2}]$$

The Analytical Model. The analytical model was found to be inconvenient for the modeling of the present system. As may be easily seen, the relative reactivity ratios r_{ij} enter into the analytical model (eqs 18–22) as reciprocal values, making the model very sensitive to small r_{ij}. Since this is the case for several r_{ij} in the present calculations and estimation errors are especially high for small r_{ij} values (see results of the TM method), results obtained by means of this model are not reliable.

The Monte Carlo Methods. This method avoids the disadvantages of the analytical model and can be additionally applied without any modifications to *n* component systems. Copolymer composition calculated in terms of this procedure was plotted in Figure 1b as a function of the monomer feed composition.

It should be emphasized that the RSC modeling was applied taking into consideration preevaluated relative reactivity ratios; i.e., the RSC model itself was not fitted to experimental data. As a result, no exact agreement between the experimental and calculated values for copolymer composition could be expected. Such neutral proceedings allowed us, however, to check the physical meaning of the relative reactivity ratios which vary with solvent, and it opens the way to more precise modeling in terms of nonlinear curve fitting. This refined modeling will lead to optimum agreement between the experimental and computed data. This modeling step is not considered in the present work and is considered to be the subject of future work.

It should be emphasized that the estimation of a part of the relative reactivity ratios depends on the viscosity of the reacting medium.[25] This is the case since the global reaction rate is subjected to evaluations and this last quantity depends on viscosity via the termination rate.

The RSC model correctly describes all tendencies observed from the experiment (Figure 1b). Copolymers obtained in c-H contain markedly more NVP than in other solvents. In NMP less NVP is inserted into the polymer than in MiB except for a very high NVP content in the feed (more than 95 mol % NVP). However, NVP contents calculated in NMP and MiB are 3–5 mol % over the measured values. This deviation is probably a result of insufficient knowledge of the relative reactivity ratios estimated above.

The superiority of the RSC modeling over the classical model lies in the possibility of describing the rather complex behavior of a binary monomer system on the basis of one set of constants estimated by independent methods. This allows a much more profound understanding of the solvent effect on the composition of copolymers synthesized in binary copolymerization. The classical model can closely describe effects observed, but it does not allow us to understand them.

Furthermore, the RSC model allows predictions of the solvent effect on the copolymer composition as in the following not yet proved example.

The copolymer composition was calculated in an excess amount of solvent complexing both MMA and NVP with $K = 0.15$. The resulting curve is presented in Figure 1b as the lowest curve (– •• –). It can be seen that such a solvent will further reduce the NVP content in the polymer.

5. Discussion

Since the relative reactivity ratios for the system MMA/NVP depend on the reaction medium, the reactivity parameters Q and e were calculated according to Alfrey and Price[26] and are tabulated below.

monomer	solvent	E_T (solvent)[a]	Q	e	ref
MMA	bulk		0.78	0.535	27
	c-H	31.2	0.36	0.75	
	MiB	37	0.67	0.94	
	NMP	42	1.11	0.63	
NVP	bulk		0.088	−0.948	27
	c-H	31.2	0.090	−1.16	
	MiB	37	0.019	−1.35	
	NMP	42	0.046	−1.04	

[a] Solvent characteristic value according to Dimroth;[28] for MiB and NMP approximate values only.[17]

Data summarized in this tabulation reveal that the solvent polarity expressed in terms of E_T changes mainly the resonance factor Q of the monomers, and to a much lesser extent the polarity parameter e. Furthermore, monomers show opposite behavior in relation to each other. The smaller the solvent polarity, the smaller are the differences between the resonance factors Q of both monomers and the better they can be copolymerized. The copolymerization curve in Figure 1a approaches the diagonal.

Conversely, with increasing solvent polarity, Q_{MMA} increases and Q_{NVP} decreases. Monomers copolymerize worse and the copolymerization curve moves away from the center of the diagram in Figure 1a.

As mentioned above Q_{MMA} and e_{MMA} were calculated, taking $Q_{NVP,bulk}$ and $e_{NVP,bulk}$ as basis and vice versa. Changes in Q and e presented above are *relative*, and they do not necessarily mean that the *absolute* Q and e values show the same tendencies. As discussed in ref 17, absolute e values of monomers will indeed change slightly with an increase of the solvent polarity. Absolute Q values increase under the same conditions generally for all monomers with a very different rate.

Growing radicals under consideration in the present paper belong to the group of nucleophilic radicals. The selectivity of such radicals depends on the interaction energy of the singly occupied molecular orbital (SOMO) of the radical with the lowest unoccupied molecular orbital (LUMO) of the monomer.

In Figure 2 energy interactions of molecular orbitals of the reacting partners are presented for two solvents with $E_{T,0} < E_{T,1}$. Increasing E_T, the reactivity of the MMA monomer increases the most rapidly (strong decrease of the LUMO energy) and the reactivity of the MMA radical reduces markedly (decrease of the MMA SOMO energy). The NVP monomer and radical behave similarly, but their MO energy changes are much less because the absolute changes in Q are considerably less than those for MMA.[17] (It is valid even if the solvent susceptibility of NVP is higher than that of MMA in the homopolymerization.[17] The absolute changes in Q are decisive.) It follows that r_{12} should increase and r_{21} should decrease with increasing E_T which stands in agreement with the experimental results.

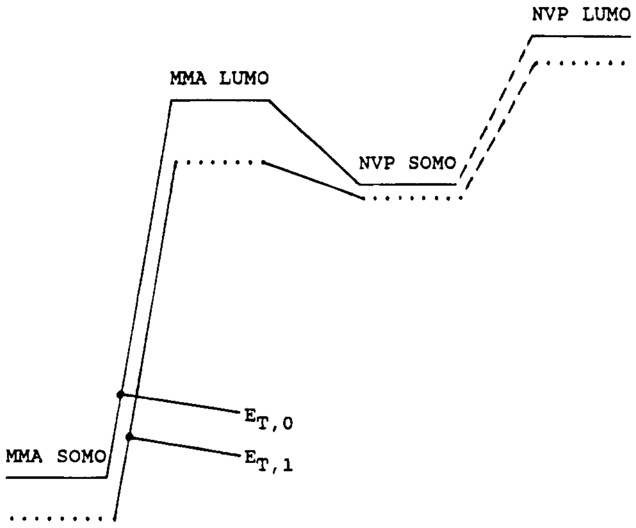


Figure 2. Scheme of the molecular orbital energies of the reacting partners in the copolymerization of MMA with NVP in two solvents with $E_{T,0} < E_{T,1}$.

Results discussed above are very consistent considering that the MMA/NVP copolymerization in cyclohexane is heterogenous. In this precipitant the copolymerization is satisfactorily described by the terminal model (Figure 1a), and the reaction rate was in exactly the same range as for other solvents. These facts allow us to expect that the heterogenous character of polymerization does not substantially influence either the selectivity of growing radicals via pronounced preferential solvation or their concentration level via cage effects. Furthermore, ^{13}C-NMR observation of the electron density at the β-C atom in MMA and NVP[25] fully supports the results presented here, especially concerning nonpolar cyclohexane as solvent. The electron shell at this atom shows the highest density in c-H; i.e., monomers exhibit the lowest reactivity in this solvent. In this connection it seems to be very probable that observed solvent effects are electronic in nature and explain why the discussion presented above is consistent.

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