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# Solvent effect on free radical polymerization: 8.* Modelling of copolymerization rate for the binary system methylmethacrylate/N-vinyl pyrrolid-2-one in different solvents

**Wojciech Krzsztof Czerwinski†**
*Deutsches Kunststoff-Institut, Schloßgartenstrasse 6, D-64289 Darmstadt, Germany*

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For the first time, modelling of the binary copolymerization rate is presented as a function of the solvent quality. This modelling was performed using a set of constant parameters only, i.e. with exclusion of variables. As an example, the copolymerization rate of the comonomer system methylmethacrylate (MMA)/N-vinyl pyrrolid-2-one (NVP) is described in terms of solvents: N-methyl pyrrolid-2-one (NMP), methyl isobutyrate (MiB) and cyclohexane (c-hex) as a function of the monomer feed composition. The polymerizations were conducted at 60°C with AIBN as initiator at a global monomer concentration of $0.4\,\mathrm{mol\,l^{-1}}$. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: free radical polymerization; copolymerization rate; solvent effect analysis)**

## *Introduction*

The reaction rate of free radical polymerization is one of the less understood quantities obtainable from this kind of reaction[1,2]. Despite the need for more knowledge of the effect of the solvent on this reaction[3], only a few systematic studies have been made at the present time[4–7] in this field. Solvents can affect, further, the composition of binary copolymers[8] and the rate of copolymerization. Until now no solvent effect related rate modelling has been given in the literature.

It has been shown that the reactant–solvent complex model (RSC model) opens a reasonable way to the basic understanding of the effect of the solvent on the propagation reaction[5–8]. For this study, solvatochromic correlation analysis has been shown to be a very powerful tool[8].

The aim of the present paper is to model the binary copolymerization rate as a function of the monomer feed composition and solvent quality. For this purpose, RSC modelling in connection with the Monte-Carlo method was used. As an example, the rate of the system methylmethacrylate (MMA)/N-vinyl pyrrolid-2-one (NVP) in the solvents N-methyl pyrrolid-2-one (NMP), methyl isobutyrate (MiB) and cyclohexane (c-hex) was subjected to calculation.

## *Theoretical*

For the simplest type of radical polymerization, i.e. considering only bimolecular termination, no induced decomposition of initiator, no degradative chain transfer reactions, the reaction rate $R_p$ of polymerization is described by equation (1) according to the hypothesis of North *et al.*[9,10]:

$$R_p = [k_p/(k_t^0)^{0.5}] \cdot \eta^{0.5}(2k_d f[\mathrm{I}])^{0.5} \cdot [\mathrm{M}] \qquad (1)$$

where $k_d$ is the initiator dissociation constant, $k_p$ the propagation rate constant, $k_t^0$ the termination rate constant independent of solvent viscosity, $\eta$ the dynamic viscosity, $f$ the initiator efficiency factor, [I] the initiator concentration and [M] the monomer concentration.

Equation (1) can be applied to describe the rate of radical polymerization processes generally, but in the case of copolymerization $k_p$, and also $k_t^0$, should be subjected to further modelling as functions of the monomer feed composition. In cases that such modelling is possible and that all other quantities are known, equation (1) represents a very simple way of describing sometimes complex reaction schemes.

The Monte-Carlo method provides a simple way of modelling $k_p$ for copolymerization and an unlimited number of comonomers. Therefore, the mean propagation constant $k_{p,\mathrm{mean}}$ results, for $n$ propagation steps between the radical $i$ and the monomer $j$, in[11]:

$$k_{p,\mathrm{mean}} = \frac{1}{\dfrac{1}{k_{p,\mathrm{mean}}}} = \frac{n}{\sum_{l=1}^{n}\left(\dfrac{1}{k_{pij}}\right)} \qquad (2)$$

In the present case, RSC modelling requires the application of the quaternary copolymerization scheme[8] ($i = 1$ to 4 and $j = 1$ to 4).

All $k_{pij}$ values can be calculated using tabular $k_{pij}$ values and corresponding relative reactivity ratios (given in standard tables for binary systems). In this case they were taken from ref. 8. The succession of the particular propagation step is determined by the Monte-Carlo procedure as discussed in this reference.

The mean value of $k_{p,\mathrm{mean}}$ was finally used as $k_p$ to calculate $R_p$ according to equation (1). For simplification, only one $k_t^0$ value was taken for all $R_p$ calculations.

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* Part 7 of this investigation is cited as ref. 8

† Present address: Silcherstrasse 22, D-22761 Hamburg, Germany

### *Results*

The experimental $R_p$ values for the system MMA/NVP polymerized in NMP, MiB and c-hex were adopted from ref. 8. The reactions were conducted at 60°C with AIBN as initiator ([AIBN] = $1.218 \times 10^{-2}$ mol l$^{-1}$) at a global monomer concentration of 0.4 mol l$^{-1}$. This concentration was also used for the calculations.

The following conditions were also considered for the calculations:

1. The initiator concentration was set to $1.218 \times 10^{-2}$ mol l$^{-1}$, corresponding to the experiments.
2. The product $2k_d f$ was set for the particular solvents as follows[12]:
   in c-hex $8.60 \times 10^{-6}$ s$^{-1}$,
   in MiB $8.41 \times 10^{-6}$ s$^{-1}$,
   in NMP $9.68 \times 10^{-6}$ s$^{-1}$.
3. It was assumed that the viscosities of the reaction mixtures do not substantially deviate from the viscosities of the solvents, because of the very low monomer concentration. The following solvent viscosities were measured at 60°C:
   c-hex 0.530 mPa s,
   MiB 0.325 mPa s,
   NMP 1.030 mPa s.
4. The following $k_{pii}$ values were used for homopropagation steps:
   for MMA: 515 l (mol s)$^{-1}$ [13]
   for NVP: 1330 l (mol s)$^{-1}$ [14].
   All other propagation rate constants were calculated using the relative reactivity increments tabulated for the system MMA/NVP in ref. 8.
5. As mentioned above, only one $k_t^0$ value was taken for all calculations. It was determined from $k_t$ values for MMA homopolymerization in bulk at 60°C as follows[13]:
   $k_t^0 = k_t \cdot \eta$ with $k_t \approx 20 \times 10^6$ l (mol s)$^{-1}$ and $\eta = 0.369$ mPa s
   $k_t^0 = 7.6 \times 10^6$ l mPa s (mol s)$^{-1}$.

In *Figure 1* the experimental reaction rate is compared in all three solvents with the calculated rate values as a function of the relative comonomer feed composition.

In the solvents under investigation the following rate succession was observed: NMP > c-hex > MiB. All other observed tendencies are interpreted correctly in terms of the theoretical modelling.

It results, from the modelling presented, that rate differences found in different solvents are due to changes of: (a) propagation rate constant $k_p$, (b) initiation rate, and (c) viscosity of the reacting system. With decreasing $R_p$ all these quantities decrease, taking into consideration the solvent succession mentioned above.

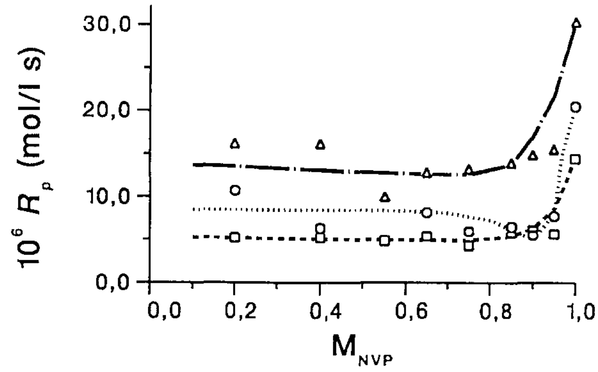

**Figure 1** Copolymerization rate of the MMA/NVP system as a function of the relative monomer feed composition obtained at 60°C with [AIBN] = $1.28 \times 10^{-2}$ mol l$^{-1}$ and [MMA] + [NVP] = 0.4 mol l$^{-1}$ in: △ —·—·— NMP; ○ ··· cyclohexane; □ - - - MiB as solvents. Curves are calculated in terms of the RSC model and the Monte-Carlo method (see text)

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