# The Kinetics of Emulsion Copolymerization of Methyl Methacrylate and Ethyl Acrylate in the Presence of Methanol

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The effect of methanol on the kinetics of the emulsion copolymerization of methyl methacrylate with ethyl acrylate, initiated by ammonium peroxodisulfate in the presence of a blend of anionic and nonionic emulsifiers was investigated at 60 °C by the conventional gravimetric method. The copolymerizations under batch conditions were conducted to both low and high conversion. It was found that methanol unexpectedly strongly reduced the rate of copolymerization which decreases with the increasing diluent concentration. The decrease of the rate of polymerization was discussed in terms of the dilution of recipe ingredients and of the desorption of radicals from polymer particles. The rate of polymerization was found to increase with increasing conversion up to 70 or 80 %. The high rate of polymerization at high conversions was ascribed to propagation of the more reactive ethyl acrylate monomer and the gel effect. The average particle diameter increases with increasing of the diluent concentration.

The kinetics of the emulsion polymerization can be divided into two stages: particle nucleation and particle growth. In the classical emulsion polymerization [1], the monomer-swollen emulsifier micelles were identified as the main locus of the particle nucleation. In another nucleation mechanism, the homogeneous particle nucleation [2, 3], the aqueous phase is the main locus of particle generation. Radicals generated in this phase grow up to a critical chain length, at which they aggregate out. The aggregated oligomer radicals absorb monomer and emulsifier to form primary particles. The particle nucleation determines the number of particles present in the system and thus the rate of polymerization. The particles growth proceeds by the propagation of monomer in polymer particles and by the association of unstable particles. The former process increases the rate of polymerization whereas the latter one reduces it.

It is known that the aggregation of oligomer radicals from the aqueous phase plays an important role in altering the polymerization process in emulsion systems. In fact, the dispersion polymerization can be regarded as an ideal case to study the nucleation mechanism; it is a special case of precipitation polymerization in which flocculation and the continuous phase type control the rate of polymerization and the particle size. The polymerization in the aqueous phase forms the insoluble polymer dispersed in the continuous phase [4]. The nature

of the continuous phase is a function of the distribution of monomer between the monomer droplets and the aqueous phase. The distribution of monomer can be regulated by the addition of a cosolvent well miscible with monomer and water.

In earlier works [5—8] of this series, we reported on the effect of the water-soluble initiator and emulsifier concentration, the emulsifier blend composition and the oil-soluble additives on the rate of polymerization, polymer molecular mass, latex stability, and the size and number of polymer particles in the emulsion copolymerization of methyl methacrylate and ethyl acrylate. In our more recent work [8] we found that oil-soluble additives reduce the rate of polymerization which decreases with the increasing diluent concentration.

In the present work the effect of methanol on the kinetics of the emulsion copolymerization of methyl methacrylate and ethyl acrylate initiated by the water-soluble initiator is studied. Methanol is well miscible with water and monomer, but acts as a precipitant of the copolymer formed. Thus, the aim of this work is to influence the properties of the continuous phase and the polymerization process by the addition of methanol.

## EXPERIMENTAL

Methyl methacrylate (MMA) and ethyl acrylate (EA) (Chemical Works, Žilina resp. Sokolovo) were purified as described in [5], Tween 40 (Tw), reagent grade (nonionic emulsifier, polyoxyethylene sorbitan

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monopalmitate, 97 % aqueous solution, Serva), Spolapon AOS (Sp) (anionic emulsifier, sodium 17-octadecenesulfonate, 40 % aqueous solution, Spolchemia), and anal. grade ammonium peroxodisulfate (AP) (Lachema, Brno) were used. Solvents as methanol, toluene, and acetone, and water as a polymerization medium were twice distilled before use.

Emulsion copolymerizations of methyl methacrylate and ethyl acrylate were carried out at 60 °C. In all runs 150 g of water, 20 g of MMA, 80 g of EA, 1.5 g of Tw, 3.5 g of Sp, 0.0094 g of $NaHCO_3$ (buffer), and 0.25 g of AP was used, amounts of methanol varied. The polymerization technique used has been described in detail elsewhere [9].

Limiting viscosity numbers [$\eta$] were measured in acetone at 30 °C. The number average molecular masses $\bar{M}_N$ were measured on a high-speed membrane osmometer 502 (Hewlett—Packard) in toluene at 30 °C. The polymer latexes were freed from monomer, initiator, methanol, and emulsifier by dialysis according to the method described in [5]. The latex particle size (effective diameter) determination, the calculation of the number of particles, and the conductivity measurements of polymer particles have been described elsewhere [10—12].

The coefficient of distribution of methanol between the monomer phase and water, and the ratio of the methanol concentration in monomer to that in water were determined from the volume change of each phase.

## RESULTS AND DISCUSSION

The conversion–time data of the emulsion copolymerization of methyl methacrylate and ethyl acrylate initiated by ammonium peroxodisulfate are shown in Fig. 1. They illustrate the effect of methanol on the course of polymerization.

Kinetic data of the emulsion copolymerization of methyl methacrylate and ethyl acrylate are also shown in Tables 1—3. The ratio of emulsifiers [Sp]/[Tw] = 3.4 and that of monomers [EA]/[MMA] = 4.0 was held. Under the present reaction conditions the stable polymer latexes were formed in both the presence and absence of methanol.

The rate of polymerization $R_p$ was determined at 10, 30, 50, and 80 % conversion, respectively. At 10 and 30 % conversions the polymer particles are saturated with monomer whereas at 50 and 80 % conversion the polymerization proceeds under the monomer-starved conditions.

A few separate regions are distinguished in the present conversion curves. The first interval is mostly located in the range of 0—10 % conversion

Table 1. Variation of the Rate of Polymerization at Emulsion Copolymerization of Ethyl Acrylate and Methyl Methacrylate without Methanol [8]

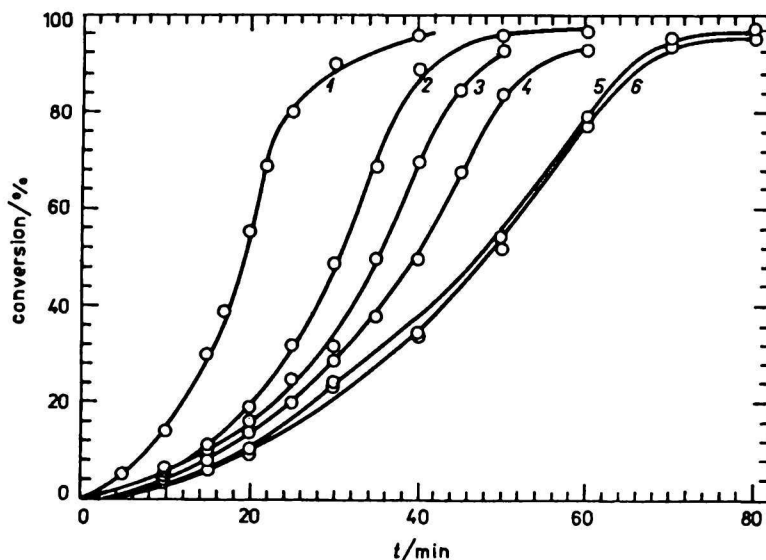| Conversion | $R_p \cdot 10^3$ | $[M]_{eq}$ | $R_{pl} \cdot 10^4$ [a] | $\bar{Q}$ |
|---|---|---|---|---|
| % | mol $dm^{-3}$ $s^{-1}$ | mol $dm^{-3}$ | $s^{-1}$ | |
| 10 | 0.9 | 7.2 | 1.2 | – |
| 20 | 2.7 | 7.2 | 3.8 | 1.9 |
| 30 | 4.4 | 7.2 | 6.1 | 3.0 |
| 40 | 5.7 | 6.0 | 9.5 | 4.6 |
| 50 | 6.7 | 5.1 | 13.0 | 6.3 |
| 60 | 6.7 | 4.1 | 16.0 | 7.9 |
| 70 | 6.7 | 3.2 | 21.0 | 10.2 |
| 80 | 3.9 | 2.1 | 19.0 | 9.0 |
| 90 | 1.4 | 1.1 | 13.0 | 6.2 |

a) $R_{pl} = R_p/[M]_{eq}$.



Fig. 1. Variation of monomer conversion in the emulsion copolymerization of ethyl acrylate and methyl methacrylate with reaction time and concentration of methanol. c(Methanol)/(mol $dm^{-3}$): 1. 0, 2. 0.21, 3. 0.63, 4. 1.04, 5. 2.08, 6. 4.16.

**Table 2.** Variation of the Rate of Polymerization at Emulsion Copolymerization of Ethyl Acrylate and Methyl Methacrylate at $c$(Methanol) = 0.21 mol dm$^{-3}$

| Conversion | $R_p \cdot 10^3$ | $[M]_{eq}$ | $R_{pf} \cdot 10^4$ | $\bar{Q}$ |
|---|---|---|---|---|
| % | mol dm$^{-3}$ s$^{-1}$ | mol dm$^{-3}$ | s$^{-1}$ | |
| 10 | 0.5 | 7.2 | 0.7 | – |
| 20 | 2.0 | 7.2 | 2.8 | 1.1 |
| 30 | 3.2 | 7.2 | 4.4 | 1.7 |
| 40 | 3.9 | 6.0 | 6.5 | 2.6 |
| 50 | 4.5 | 5.1 | 8.8 | 3.6 |
| 60 | 4.8 | 4.1 | 11.7 | 4.8 |
| 70 | 5.4 | 3.2 | 16.9 | 6.8 |
| 80 | 3.9 | 2.1 | 18.9 | 7.6 |
| 90 | 2.0 | 1.1 | 18.1 | 7.3 |

**Table 3.** Variation of the Rate of Polymerization at Emulsion Copolymerization of Ethyl Acrylate and Methyl Methacrylate at $c$(Methanol) = 2.08 mol dm$^{-3}$

| Conversion | $R_p \cdot 10^3$ | $[M]_{eq}$ | $R_{pf} \cdot 10^4$ | $\bar{Q}$ |
|---|---|---|---|---|
| % | mol dm$^{-3}$ s$^{-1}$ | mol dm$^{-3}$ | s$^{-1}$ | |
| 10 | 0.4 | 7.1 | 0.6 | – |
| 20 | 1.1 | 7.1 | 1.5 | 0.8 |
| 30 | 1.6 | 7.1 | 2.2 | 1.1 |
| 40 | 1.8 | 6.0 | 3.0 | 1.6 |
| 50 | 2.2 | 5.0 | 4.4 | 2.2 |
| 60 | 2.5 | 4.0 | 6.2 | 3.2 |
| 70 | 2.7 | 3.2 | 8.4 | 4.4 |
| 80 | 2.8 | 2.1 | 13.3 | 6.9 |
| 90 | 1.3 | 1.1 | 11.8 | 6.2 |

(the nucleation stage), the stationary state interval (interval 2) within 15—70 % or 80 % conversion and the last interval 3 above 70 or 80 % conversion. Such a behaviour is the direct result of the generation of polymer particles, their growth, and the polymerization under the monomer-starved conditions.

The experimental data in Tables 1—3 show the increase of the rate of polymerization $R_p$ with increasing conversion up to 70 or 80 %. In the first interval the rate of polymerization increases strongly with conversion. The addition of methanol increases the duration of the nucleation period. The continuous water—methanol phase saturated with higher monomer concentration favours more the homogeneous polymerization. The formation of new particles thus is expected to increase with increasing the water-soluble monomer concentration.

The equilibrium monomer concentration $[M]_{eq}$ for the emulsion copolymerization of ethyl acrylate and methyl methacrylate was reported to be ca. 7.2 mol dm$^{-3}$ [8, 11]. The monomer droplets thus should deplete at 30 % conversion at which the rate of polymerization should reach the maximum. Tables 1—3 however show that the maximum rate appears at 70 or 80 % conversion. After the deple-

tion of monomer droplets the monomer concentrates in the continuous and polymer particle phases. Over the intervals 2 and 3, the continuous phase may only partly saturate the polymer particles with monomer while the amount of water-soluble monomer is restricted [13]. After the depletion of monomer droplets the continuous phase may saturate the polymer particles in the further 20 % conversion at the most. The authors [13] however reported that the amount of water-soluble monomer after the depletion of monomer droplets linearly decreases with increasing conversion. At high conversions the polymerization proceeds under monomer-starved conditions.

The high rate of polymerization at high conversion should be discussed in terms of the gel effect. In favour of this idea is the increase of the polymer volume fraction in polymer particles. It is known that the high volume fraction of polymer raises the viscosity of the reaction system. When the gel effect is operative, it leads to a sharp decrease in the termination rate constant $k_t$.

It is generally recognized that acrylates and methacrylates exhibit a "strong" gel effect [14—16]. *Manyarai* and *Patra* [15] observed a strong gel effect at very low conversion in the bulk polymerization of ethyl acrylate. The onset of the gel effect in the bulk polymerization of methyl methacrylate was observed also at very low conversion ($\approx$ 10 %) [16]. In the emulsion polymerization of methyl methacrylate, *Parker* and *Piirma* [17] observed the strong gel effect above ca. 50 % conversion. Thus, the gel effect appeared after the depletion of monomer droplets.

The gel effect seems to be operative also in the emulsion copolymerization of ethyl acrylate and methyl methacrylate. It increases the rate of polymerization after the depletion of monomer droplets even if the concentration of monomer in the continuous and polymer particle phases decreases. The strong acceleration of polymerization is visualized from 30 or 40 % up to 70 or 80 % conversion. At the higher conversion the monomer concentration is very low and the system reaches slowly the glassy state. Here the propagation reaction as well as the entry of the initiating radicals is restricted. The rate of both processes is regulated by the monomer diffusion.

The formation of the high-molecular mass polymers increases not only the inner viscosity, but also the fraction of entangled macromolecules. Because the free volume remains relatively high through the reaction (due to the low $T_g = -54$ °C) and cannot explain this strong gel effect, entanglement coupling should be the main driving force for the acceleration of ethyl acrylate polymerization [18]. In the case of methyl methacrylate the free

**Table 4.** Variation of the Rate of Polymerization at Emulsion Copolymerization of Ethyl Acrylate and Methyl Methacrylate with Methanol Concentration

| Run | $c$(Methanol) $\overline{\text{mol dm}^{-3}}$ | $R_p \cdot 10^3$ $\overline{\text{mol dm}^{-3}\text{ s}^{-1}}$ | | | | | $R_p/R_{p0}$ | | $R_{pp} \cdot 10^{20}$ * $\overline{\text{mol s}^{-1}}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | $a$ | $b$ | $c$ | $d$ | $e$ | $a$ | $c$ | $c$ |
| 1 | 0 | 0.9 | 4.4 | 6.7 | 3.9 | 6.7 | 1.0 | 1.0 | 4.1 |
| 2 | 0.21 | 0.6 | 3.2 | 4.5 | 3.9 | 4.6 | 0.66 | 0.67 | 3.2 |
| 3 | 0.63 | 0.5 | 2.4 | 3.7 | 3.0 | 3.9 | 0.55 | 0.55 | 2.8 |
| 4 | 1.04 | 0.4 | 2.5 | 3.2 | 2.5 | 3.4 | 0.44 | 0.48 | 2.5 |
| 5 | 2.08 | 0.4 | 1.6 | 2.2 | 2.8 | 2.6 | 0.44 | 0.33 | 2.0 |
| 6 | 4.16 | 0.4 | 1.7 | 2.3 | 2.7 | 2.8 | 0.44 | 0.34 | 2.2 |

\* The average rate per particle $R_{pp}$ (the corresponding number of particles is presented in Table 5). a) At 10 % conversion, b) 30 %, c) 50 %, d) 80 %, e) corrections of the rate of polymerization (data from the column c) on the dilution of initiator, emulsifier, and monomer.

volume effect (due to the high $T_g$ = 115 °C) and the entanglement coupling produce the profound gel effect. Hence the onset of the gel effect in the bulk polymerization of methyl methacrylate was observed at very low conversions [16]. At this gel point the number average molecular mass $\overline{M}_N$ was reported to be $ca.$ 1.4 x $10^6$, $i.e.$ the polymer chains with molecular mass above this value were regarded as entangled and thus of restricted mobility [16].

Reactivity ratios of methyl methacrylate and ethyl acrylate monomer couple, $r_{MMA}$ = 2.52 and $r_{EA}$ = 0.16 [19], indicate that at low and medium conversion copolymer is enriched with methyl methacrylate and at high conversion with ethyl acrylate. The gel effect appears at high conversion while the polymer particles contain also the high amount of ethyl acrylate monomer. Here the high propagation rate constant of ethyl acrylate governs the polymerization process.

Table 4 shows the strong decrease of the rate of polymerization with the increasing methanol concentration. Methanol is well miscible with water and monomer, hence it divides the reaction ingredients into the aqueous and monomer phases. The distribution coefficient of methanol between the monomer phase (100 $cm^3$) and water (150 $cm^3$) is found to be 0.5. This value indicates that methanol increases also the solubility of monomer in water and decreases the amount of monomer in the polymer particles. Corrections of the rate of polymerization on the dilution of initiator, emulsifier and monomer, however, showed that the corrected rates differ only slightly from the uncorrected ones even if the very high diluent concentration was used. Hence, the dilution itself does not explain the decrease of the rate of polymerization. The decrease of the rate of polymerization with increasing diluent concentration cannot be discussed in terms of the decrease of the decomposition rate of peroxodisulfate whereas the ionic strength of the continuous phase is the same in all systems.

The solubility of anionic emulsifiers in water is very high in contrast to that of nonionic emulsifiers [20]. The nonionic emulsifiers are mostly highly soluble in the oil (monomer) phase [21, 22]. With increasing of the methanol concentration the micellar fraction of both anionic and nonionic emulsifiers decreases. Hence, the total amount of emulsifier available for the formation and stabilization of polymer particles decreases.

If the copolymerization is carried out without diluent, a largest amount of both emulsifiers is "stored" in the micellar form [21, 22]. In the reaction system charged with high concentration of methanol the critical concentration of emulsifier and its concentration in the monomer phase increases. The increase of the nonmicellar fraction of emulsifier favours the formation and the growth of large polymer particles with lower stability. In favour of this idea is the dependence of size or the number of particles on methanol concentration (Table 5). Here the average particle diameter $\overline{d}$ increases and the number of particles $N$ in aqueous phase decreases with the increasing methanol concentration. In the emulsion polymerization of styrene the increase of the particle size was attributed to the increased solubility of styrene in the presence of the hydrophilic agent, so that styrene competes for radicals more in the polymerization in water [22]. Increasing of the average polymer particle diameter results in the decrease

**Table 5.** Properties of Final Methyl Methacrylate—Ethyl Acrylate Copolymer Latexes

| $c$(Methanol) $\overline{\text{mol dm}^{-3}}$ | $\overline{d}$ $\overline{\text{nm}}$ | $N \cdot 10^{-14}$ $\overline{\text{cm}^3}$ | $[\eta]$ $\overline{\text{cm}^3\text{ g}^{-1}}$ | $\overline{M}_N \cdot 10^{-6}$ |
|---|---|---|---|---|
| 0 | 190 | 1.93 | 480 | 0.4 |
| 0.21 | 200 | 1.41 | 490 | 0.45 |
| 0.63 | 205 | 1.31 | – | 1.05 |
| 1.04 | 207 | 1.27 | – | 1.0 |
| 2.08 | 218 | 1.09 | 500 | 1.0 |
| 4.16 | 220 | 1.06 | 495 | 0.5 |

**Table 6.** Chain Transfer Constants $C_s$ [24] and the Water Solubility of Some Reactants

| MeOH | $C_s(EA) \cdot 10^4$ | $C_s(MMA)$ | $c$(Reactant) |
|---|---|---|---|
| | $(\theta/°C)$ | $(\theta/°C)$ | mol dm$^{-3}$ |
| without | 0.332 (65) | 0.2 (65) | 0.15 [25] |
| with | 0.32 (60) | 0.2 (60) | miscible |

of the total particle surface area, the fraction of radicals captured by the polymer particles, and the rate of polymerization as it was reported [23].

The high water solubility of ethyl acrylate and methyl methacrylate monomers (Table 6) gives rise to the water-phase polymerization which influences the molecular mass of the oligomer radicals as well as the number of primary particles. The addition of methanol was found to increase the water solubility of monomers as well as of monomeric and oligomeric radicals [26]. The separation of polymer radicals from water takes place above the critical degree of polymerization $X_{cr}$. In the emulsion polymerization of methyl methacrylate the separation of propagating radicals from water occurs above the value of $X_{cr} = 65$ [23]. In the presence of methanol $X_{cr}$ should increase above the value 65. The same water solubility of methyl methacrylate and ethyl acrylate ($\approx 0.15$ mol dm$^{-3}$ [25]) favours the formation of oligomer radicals with the same $X_{cr}$ for both monomers.

The water—methanol phase polymerization resembles the precipitation polymerization. In such a process the growth of polymer particles is governed by the coagulative mechanism [27]. The results of polymerization under individual reaction conditions are given in Tables 1—3.

In the light of micellar and homogeneous nucleation theories [1—3] the rate of polymerization is proportional to the equilibrium monomer concentration, $R_p \sim [M]_{eq}$, then $R_{p0}/R_{px} = [M]_{eq0}/[M]_{eqx}$ should hold ($R_{p0}$, $R_{px}$ are the rates of polymerization in the absence and in the presence of methanol).

Actually, in the system with $c$(methanol) = 0.21 mol dm$^{-3}$ $R_{p0}/R_{p1} = 1.4$ (at 30 % conversion) and 1.5 (at 50 % conversion) and $[M]_{eq0}/[M]_{eq1} = 1$ (at 30 and 50 % conversion), in the system with $c$(methanol) = 2.08 mol dm$^{-3}$ $R_{p0}/R_{p2} = 2.8$ (at 30 % conversion) and 3.0 (at 50 % conversion) and $[M]_{eq0}/[M]_{eq2} = 1$ (at 30 and 50 % conversion).

These results, thus, deviate from the theories [1—3]. The abrupt decrease in the rate of polymerization by the addition of a small amount of methanol indicates that some other factors, such as the radical desorption and the chain transfer influence the polymerization process.

Generally the depletion of monomer droplets occurs ca. at 30—50 % conversions. At these conversions the maximum of the fractional rate $R_{pf}$ defined by the ratio between the rate of polymerization and the monomer concentration usually appears [9, 28]. In the homogeneous polymerizations, on the contrary, the fractional rate is constant, except of very low and high conversions. In the present study the fractional rate increases with increasing conversion and reaches the maximum until at 70 or 80 % conversion (Tables 1 and 2). From these data it follows that methanol does not influence the position of the maximum but influences the values of the fractional rate. The increase of the fractional rate with increasing conversion may be discussed in terms of the radical activity and the increase of the fraction of polymer particles.

Some information about the radical activity of polymer particles one can obtain from the equation for the emulsion polymerization

$$R_p = k_p[M]_{eq}\overline{Q}\,(N/N_A) \qquad (1)$$

where $k_p$ is the propagation rate constant, $[M]_{eq}$ the equilibrium monomer concentration, $N_A$ Avogadro's constant, $N$ and $\overline{Q}$ are the number of particles per unit volume and the average number of radicals per particle. For the emulsion copolymerization of monomers A (MMA) and B (EA) the rate can be expressed by the relation

$$R_p = \frac{k_{pAA}k_{pBB}N[M]_{eq}\overline{Q}(r_A + 2L + r_BL^2)}{N_A(k_{pBB}r_A + k_{pAA}r_BL)(1 + L)} \qquad (2)$$

where $r_A$ and $r_B$ are the reactivity ratios of the comonomer pair, $k_{pAA}$ and $k_{pBB}$ are the propagation rate constants and $L$ is the monomers concentration ratio [B]/[A]. From experimental values of $R_p$, $N$, $[M]_{eq}$, $r_A$, $r_B$, $k_{pAA}$, and $k_{pBB}$ the value of the average number of radicals per particle $\overline{Q}$ was calculated for run 1, 5, and 6 (Table 4) from eqn (2). For these calculations the values of $L = 4.0$, $r_A = 2.52$ and $r_B = 0.16$ [19], $k_{pAA} = 6.86 \times 10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$ [29] and $k_{pBB} = 1.5 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ [18, 24] were used. The value of $\overline{Q}$ was estimated to be 5.6 for the run 1, 1.7 for the run 5 and 0.8 for 6. The magnitude of $\overline{Q}$ for particles in the absence of diluent agrees very well with that found by Gardon [11] being as high as 5 per poly(methyl methacrylate) particle. On the other hand, the addition of methanol strongly decreases $\overline{Q}$ The value of $\overline{Q}$ for particle without diluent is in both cases 3.3 or 5 times higher than that in the run 5 or 6. Hence the decrease of the radical activity in polymer particles caused by the desorption of radicals from polymer particles depresses the rate of polymerization.

In the aqueous polymerization of methyl methacrylate the addition of methanol (5 vol. %) is found to depress the final conversion, the initial rate of polymerization as well as the molecular mass of polymer [30]. This behaviour was ascribed to the decrease of colloidal stability. The polymerization of methyl methacrylate in binary or ternary systems composed of monomer—(solvent)—precipitant of the polymer showed that the termination rate constant increases with the decreasing solvent power [31]. With increasing conversion the volume fraction of methanol is constant while that of monomer decreases [32]. The solvent power within the polymer particles decreases with the increasing diluent concentration. Thus, the rate constant of termination $k_t$ is also responsible for the rise of the fractional rate of polymerization with increasing conversion. Methanol worsens the thermodynamic quality of reaction media within the polymer particles (mixture of monomer with diluent) and favours the formation of occluded radicals.

At the first sight the chain transfer to methanol should not contribute to the decrease of the rate of polymerization while the chain transfer constants for methanol are the same or lower than those for ethyl acrylate or methyl methacrylate monomer (Table 6). The chain transfer to methanol is postulated, however, to produce the hydrophilic methanol radicals with high affinity to water. Hence the dilution of monomer by methanol increases the exit rate of diluent radicals from polymer particles and the period in which monomer addition occurs increases. The desorption of radicals is known to reduce the average number of radicals per particle, the rate of polymerization and radical activity of polymer particles [33]. In favour of the radical desorption seems to be the decrease of the ratio $R_p/R_{p0}$ with increasing methanol concentration (Table 4).

At very low and high conversions the molecular mass of copolymers is independent of the methanol concentration (Table 5). Using the medium methanol concentration the polymers with higher molecular mass were formed.

The stability of polymer particles was independent of the methanol concentration in the range of low and medium diluent concentrations. In the system with the high methanol concentration the stability of the polymer latex slightly decreases. It results from the fact that with increasing methanol concentration the micellar concentration of emulsifier decreases (Table 7).

The conductivity $\kappa$ of the latexes, however, decreases with the increasing methanol concentration (Table 7). This indicates that the diluent molecules favour the "tying-up" the conductive species from the water phase. In favour of this idea are the

**Table 7.** Properties of Final Methyl Methacrylate—Ethyl Acrylate Copolymer Latexes

| c(Methanol) | $\kappa$ | w(Coagulum)[a] |
|---|---|---|
| mol dm$^{-3}$ | mS cm$^{-1}$ | % |
| 0 | 1.1 | 1.0 |
| 0.21 | 0.9 | 1.0 |
| 0.63 | 0.9 | 1.0 |
| 1.04 | 0.8 | 0.0 |
| 2.08 | 0.8 | 0.0 |
| 4.16 | 0.6 | 3.0 |

a) Coagulum at the end of polymerization.

results obtained in the presence of the lower 1-alkanols ($C_2$—$C_7$) [34]. Small amounts of these alkanols usually stabilize emulsifier micelles as evidenced by the depression of the critical micellar concentration, whereas at higher additive concentrations the micellization process becomes less favoured, until at very high contents of water-soluble alcohols micelles are not formed any more. At higher methanol concentrations, the nonmicellar form of emulsifier should increase, whereas the number of monomer-swollen emulsifier micelles should decrease. Under such conditions the formation of particles by micellar mechanism [1] and the efficiency of emulsifier as a stabilizer of polymer particles decreases.

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# Preparation of 2,4-Dichlorobenzoyl-Substituted Isoxazolines and Isoxazoles

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The synthesis of 2,4-dichlorobenzoyl-substituted isoxazolines and isoxazoles through the 1,3-dipolar cycloaddition of 2,4-dichlorobenzoylnitrile oxide is described. The regio- and stereoselectivity of the nitrile oxide cycloaddition with alkenes, alkynes, and oxygen-containing heterocycles is discussed. 2,4-Dichlorobenzoylnitrile oxide reacts with allylamine and yields the unexpected open-chain *N*-substituted amide oxime *XIV* and amide *XV*.

2,4-Dichloroacetophenone is a versatile and important intermediate for the preparation of biologically effective compounds. The 2,4-dichlorobenzoyl building block [1—3] is a characteristic feature of some commercial agrochemicals and drugs, and therefore as a part of research into applications of the 1,3-dipolar cycloadditions to the synthesis of antifungal compounds, we have made use of products originating from 1,3-dipolar cycloadditions leading to isoxazolines and isoxazoles substituted by the afore-mentioned building block. So far, only one example of the 1,3-dipolar cycloaddition of 2,4-dichlorobenzoylnitrile oxide on 3-butyn-1-ol has been reported [4]; this paper describes the reactivity and regio- and stereoselectivity of nitrile oxide *I* in 1,3-dipolar cycloaddition to some alkenes, alkynes, and oxygen-containing heterocycles.

2,4-Dichlorobenzoylnitrile oxide (*I*) was generated *in situ* from 2,4-dichlorophenylglyoxylohydroximoyl chloride (*II*, see Ref. [5]) and triethylamine in the presence of dipolarophiles. Cycloaddition of the nitrile oxide *I* to various alkenes such as allyl alcohol, allyl bromide, allyl cyanide, hexene, ethyl 2-propenoate, and styrene was regioselective and gave 5-substituted 3-(2,4-dichlorobenzoyl)isoxazolines *IIIa—IIIg* (Scheme 1) in modest yields (Table 1). The structure of *IIIa—IIIg* was determined by comparing the chemical shift data for H-5 methine and H-4 methylene protons with those published for the analogous 3-phenyl-substituted derivatives *III* [6] and by analyses of the $^{13}$C NMR spectra. The individual signals were ascribed by means of *J*-resolved and heterocorrelated NMR spectroscopy.

Dipolar cycloadditions to monosubstituted alkenes led mainly to 5-substituted isoxazolines [7]. The FMO theory predicts [8] that 4-substituted regioisomers should be obtained where there is greater frontier interaction HOMO(dipole)—LUMO(dipolarophile). Substitution at the 1,3-dipole