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# Cyclodextrins in Polymer Synthesis: Free Radical Polymerization of a *tert*-Butylmethacrylate-Cyclodextrin Host-Guest System in Aqueous Medium

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# Cyclodextrins in Polymer Synthesis: Free Radical Polymerization of a *tert*-Butylmethacrylate-Cyclodextrin Host–Guest System in Aqueous Medium

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## ABSTRACT

The homopolymerization of methylated-β-cyclodextrin (me-β-CD) host–guest compound of *tert*-butyl methacrylate (1a) is described. We investigated the free radical polymerization of the complexed monomer (1a) and of the free monomer (1) at ambient and high temperature. Poly(*tert*-butylmethacrylate) synthesized *via* the cyclodextrin mediated method exhibited number-average molecular weights ranging from 12,000–60,000 g/mol with polydispersities from 1.9–3.1. The polymerizations without cyclodextrin show significantly lower yields in comparison with the cyclodextrin mediated polymerizations. Here, the polymer obtained is colloidal dispersed. At ambient temperature (20°C) no polymerization occurs in the absence of cyclodextrin, whereas, under the same conditions, the homopolymerization of the complexed monomer (1a) leads to polymerization with yields around 75%.

*Key Words:* *tert*-Butylmethacrylate; Poly-*tert*-butylmethacrylate; β-cyclodextrin complex; Radical polymerization.

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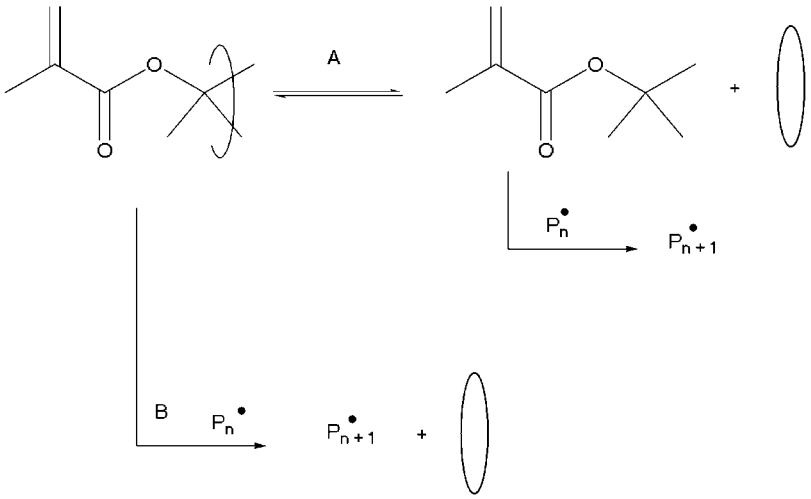
## INTRODUCTION

For the development of environmentally friendly polymerization processes, for example organic solvents are preferably replaced by water. To reduce energy consumption of industrial processes reactions at ambient temperature and at normal pressure are of great advantage. An alternative to the use of organic solvents, we have recently established a new method dealing with the free radical polymerization of cyclodextrin complexed monomers in aqueous phase. Cyclodextrins exhibits a torus-shaped structure with a hydrophobic cavity and a hydrophilic outer side. Due to this structure they are able to enclose suitable hydrophobic molecules to form host–guest compounds, in which the hydrophobic guest molecule is encapsulated fully or partially by the cyclodextrin.[1,2]

We have shown that the host/guest complexes consisting of 2,6-dimethyl-β-cyclodextrin (me-β-CD) and monomers as e.g. styrene or (meth)acrylates generally are clearly soluble in water and can be readily polymerized yielding water insoluble polymers in high yields.[3–14] Upon polymerization the polymers normally precipitate from the solution which means that the system becomes heterogeneous after a few seconds. However, up to now the mechanism of this type of polymerization is not fully understood. Moreover, cyclodextrins were used to examine their influence on emulsion polymerization.[15–17] For example, Rimmer and coworkers[18] have recently investigated the emulsion polymerization of n-butyl methacrylate with β-cyclodextrin in place of a surfactant. They supposed a new type of colloidal stabilization for their polymerizations because of the unexpected independence of molecular weight and particle size from β-CD concentration. In general they obtained the polymers as lattices. Harada et al.[19] have recently established the strong affinity of β-cyclodextrin to polymer anchored *tert*-butyl-groups. They synthesized a water insoluble copolymer from acrylamide and *tert*-butyl methacrylate in a molar ratio of 5:1. After the addition of β-cyclodextrin this insoluble polymer became solubilized. For the *tert*-butyl-group an association constant of $340\,M^{-1}$ was measured. Contrary to that, β-cyclodextrin does not include a n-butyl moiety of an copolymer of acrylamide and n-butyl methacrylate. Madison et al.[20] have reported some preliminary data about the free radical polymerization in aqueous phase of cyclodextrin complexed *tert*-butyl methacrylate. They achieved the formation of host/guest complexes with chloroform as co-solvent. After evaporation of the organic solvent they only polymerized the water soluble complexes in aqueous medium using radical initiation at 50°C and 60°C. They also investigated the stereoregularity of polymerization for the host/guest complexes. Jerome et al.[21] investigated the effect of sodium nitrite and ascorbic acid on the free radical polymerization of *tert*-butyl methacrylate in water at 80°C without me-β-CD. The behavior of this monomer at ambient temperature has not been studied. In this work, we thus wish to present for the first time our investigations on temperature sensitivity of free radical polymerization of *tert*-butyl methacrylate complexed with me-β-CD and, for comparison, also the behavior of uncomplexed *tert*-butyl methacrylate in aqueous medium under similar conditions.

Up to now, a contrary discussion came up about the mechanism of chain growing process during polymerization of cyclodextrin-complexed monomers. In this work we also want to elucidate the proposed mechanism schematically represented in Sch. 1.




***Scheme 1.*** Chain growth of polymeric radical $P_n^*$ via decomplexed monomers (A) or alternatively chain growth via the complexed monomers (B).



## EXPERIMENTAL

*Tert*-butyl methacrylate, which was obtained by Sigma-Aldrich-Chemie GmbH, Taufkirchen, FRG, was used after distillation. The methylated-β-cyclodextrin (me-β-CD) was obtained from Wacker-Chemie GmbH, Burghausen, FRG, with an average degree of methylation of about 1.8 per glucose unit. Potassium persulfate and sodium disulfite were of reagent grade and were used as received from Acros, Organics N.V./S.A., Geel, Belgium. 2,2′-azobis(amidinopropane)dihydrochloride (VA044) was obtained from Wako Chemicals GmbH, Kastellaun, FRG. Deuterium oxide (99.9 atom-% deuterium) and chloroform-$d_1$ (99.8 atom-% deuterium) were purchased from Deutero GmbH, Kastellaun, FRG. The $^1$H-NMR and 2D-ROESY spectra of the host/guest complex were recorded on a Bruker Advance DRX500 spectrometer (20°C) with DSS as internal standard. The $^1$H-NMR spectra of the polymers were recorded on a Bruker AC 200 (20°C). Thin Layer Chromatography (TLC) was carried out on Merck Silica plates (60 $F_{254}$) using methanol as solvent. The spots were visualized by UV fluorescence and by developing with $I_2$. SEC measurements were performed with a setup of the company PSS with dimethylformamide as eluent at 25°C and toluene as internal standard. Calibration was done with polystyrene-standards (PSS) ranging from 374 to 1000000 D molecular weight (flow rate of 1 mL/min). 150 μL of a 0.125 weight-% polymer solution were given onto a column combination consisting of a Hema 10 μm pre-column (40 Å) and a set of Hema 10 μm as analytical columns (40, 100, 3000 Å porosity). Detection of the signals was performed with a TSP UV2000 UV–VIS-detector (254 nm) and a modified Knauer RI-detector. Differential Scanning Calorimetry (DSC) was performed with a Perkin Elmer DSC7. The FT-IR spectra were recorded on a Nicolet FTIR-5 SXB, ATR-unit. UV measurements were conducted on an Unicam UV 540 system. Molecular modeling was done with PC Spartan

Pro, version 1.07. The PM3 method was used for geometry optimization. The effect of the solvent is not considered.

## UV-Difference Spectroscopy for Determination of Host–Guest Binding Constant K

In UV difference spectroscopy, the absorbance spectrum of an unbound substrate is measured and subtracted from its spectra at several cyclodextrin concentrations. The binding constant K is then obtained from a Benesi–Hildebrand or double-reciprocal plot based on Eq. (1).[22]

$$\left(\frac{b}{\Delta A_{obs}}\right) = \frac{1}{S_t K_{11} \Delta\varepsilon_{11} L} + \frac{1}{S_t \Delta\varepsilon_{11}} \quad (1)$$

$\Delta A_{obs}$ is the observed absorbance difference, at some particular wavelength λ, between the me-β-CD-guest complex and the free guest at different CD concentrations. $\Delta\varepsilon_{11}$ is the absorbance difference at λ between the analyte–CD complex and the free analyte. L is the molecular concentration of me-β-CD, $S_t$ the molecular concentration of the analyte, K is the binding constant and b is the path length.[23] The absorption spectrum of me-β-CD changes with addition of monomer (1). The maximum absorption of 1.49 at 191.2 nm changes to 1.71 at 190.6 nm (Fig. 1). The shoulder in the absorption curve is evoked by (1), which might be partly solved and partly complexed.

The concentration of the monomer for determination of the binding constant is $4.57 \cdot 10^{-4}$ mol/L. The water solubility of (1) was determined to $1.69 \cdot 10^{-3}$ mol/L. The analyte is solved completely in the water phase. This is necessary in order to measure the absorption spectra of (1) in pure water. A wavelength is selected at which the molar absorptivity of substrate and of complex is different. For the determination of K we

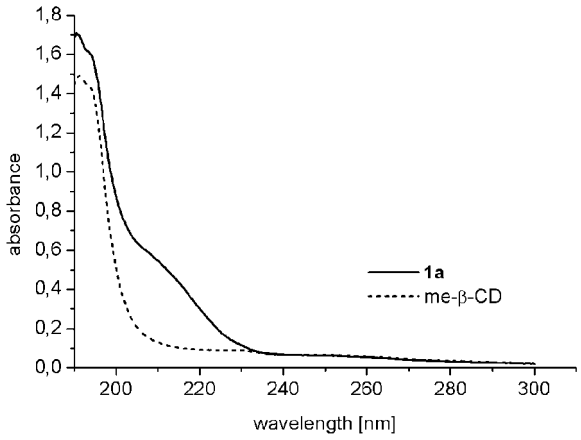



***Figure 1.*** Comparison of absorbance spectra of me-β-CD and complex (1a) (concentration of me-β-CD in both cases = $1.144 \cdot 10^{-2}$ M).

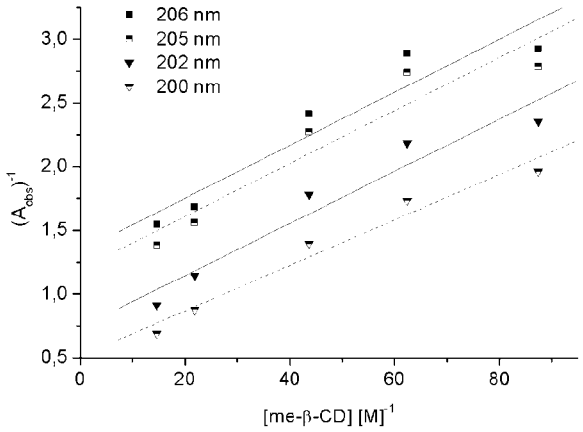



***Figure 2.*** Benesi–Hildebrand plot for complexation of monomer (1).



selected the wavelengths 206, 205 and 202 nm. Figure 2 shows the corresponding Benesi–Hildebrand-plot.

## Complexation of Monomer

19.2 g (14.6 mmol) of me-β-CD were dissolved in 64 ml of deionized water and 1.37 g (9.6 mmol) of (1) were added. The colorless dispersion was stirred for 30 min yielding a clear colorless solution of the complexed monomer (1a). Table 1 shows the characterization of the uncomplexed (1) and complexed monomer (1a).

1: $^1$H-NMR ($D_2O$, 500 MHz): δ [ppm] 6.00, 5.60 (s, $CH_2$═C($CH_3$)—); 1.85 (s, $CH_2$═C($CH_3$)—); 1.47 (s, —C($CH_3$)$_3$)

1a: $^1$H-NMR ($D_2O$, 500 MHz): δ [ppm] 5.90, 5.69 ($CH_2$═C($CH_3$)—); 1.87 (s, $CH_2$═C($CH_3$)—); 1.60 (s, —C($CH_3$)$_3$)

## Polymerization of Complex (1a) in Water

In general, the homopolymerizations were realized by initiation of the previous formed water-soluble complex (1a) by applying a molar ratio of (1)/me-β-CD of 1/1.5. For example, we introduce 1.37 g (9.6 mmol) of (1) in a solution of 19.2 g (14.6 mmol) me-β-CD in 64 mL water. The solution described above was stirred under nitrogen atmosphere at room temperature. If necessary, the solution was heated to 80°C. A certain volume of the prepared initiator-solution was added. The polymerization was terminated by cooling the reaction mixture in an ice bath and by introducing oxygen. The solid precipitate was filtered off, and washed three times with 20 mL of water. After dissolving the crude polymer in 2 ml of THF the solutions was poured into 50 ml of water. The precipitated polymer was filtered and dried *in vacuo* for 24 h. The obtained colorless polymeric product

was free of monomer according to NMR spectroscopy. To remove residual me-β-CD the polymer was extracted again with water.

Poly(*tert*-butylmethacrylate) (2): $^1$H-NMR ($CDCl_3$-$d_1$, 200 MHz): δ [ppm] 2.2–1.6 (—C$H_2$— chain); 1.6–1.2 (—C(C$H_3$)$_3$); 1.2–0.7 (—C$H_3$)

FT-IR (ATR, $\tilde{\nu}$ [$cm^{-1}$]): 2977, 2933 ($\nu_{as,s}$ CH stretching aliphatic); 1723 (C═O stretching); 1478, 1458 ($\nu_{as}$ CH aliphatic); 1393, 1368 ($\nu_s C(CH_3)_3$); 1252, 1140.

## Polymerization of Uncomplexed Monomer (1) in Water

The polymerizations without me-β-CD were realized in the same way as described above. The solutions of colloidal dispersed polymer were treated with a saturated solution of sodium chloride. After aggregation it is possible to obtain the polymers by centrifugation, yielding colorless polymeric products.

Poly(*tert*-butylmethacrylate) (2b): $^1$H-NMR ($CDCl_3$-$d_1$, 200 MHz): δ [ppm] 2.3–1.6 (—C$H_2$— chain); 1.6–1.2 (—C(C$H_3$)$_3$); 1.2–0.6 (—C$H_3$)

FT-IR (ATR, $\tilde{\nu}$ [$cm^{-1}$]): 2975, 2932 ($\nu_{as,s}$ CH stretching aliphatic); 1718 (C═O stretching); 1476, 1457 ($\nu_{as}$ CH aliphatic); 1392, 1366 ($\nu_s$ C(C$H_3$)$_3$); 1256, 1132.



## Determination of Water Solubility

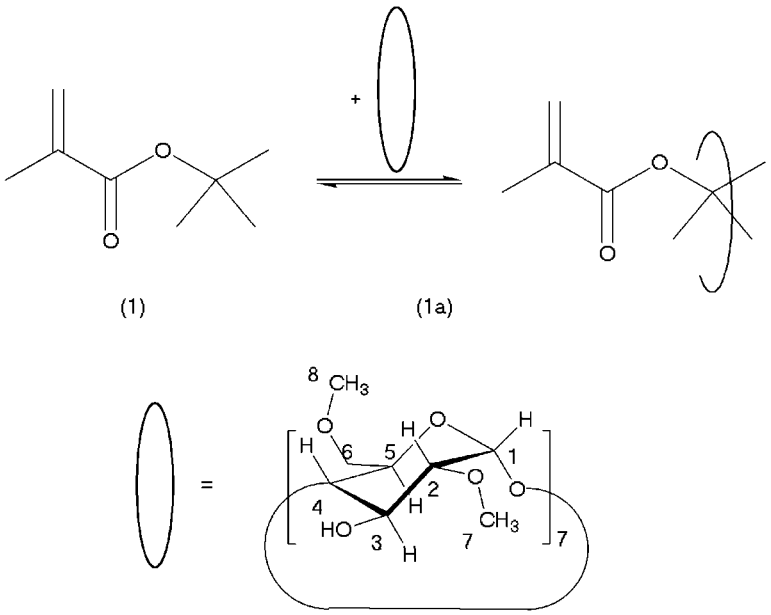
The water solubility was determined by UV spectroscopy. 0.1 mL of (1) and 19.9 mL of water were shaken in a separating funnel for 10 min. After this time, 5 mL of the mixture was dropped into a flask. A volume of 0.1 mL was diluted to 10 mL with acetonitrile/water 70/30 v/v. By linear square analyze the dependence of absorbance of the monomer-concentration was determined.

## RESULTS AND DISCUSSION

2,6-Dimethyl-β-cyclodextrin (me-β-CD) and the hydrophobic monomer *tert*-butyl methacrylate (1) were mixed in water in a molar ratio of 1.5:1 yielding a water-soluble host/guest complex after stirring for 30 min. The complexation is illustrated in Sch. 2. The complex formation was verified by thin layer chromatography. The $R_f$ value of the complex (1a) and of the free monomer (1) differ significantly from each other (Table 1).

Characterization of the complexed monomer by means of $^1$H-NMR spectroscopy was carried out. In comparison with the free monomer, the resonances of the host/guest complex are significantly shifted (Table 2).

The environment around the hydrogen atoms in the cavity changes with association of the guest molecule. A small shift in the peaks for the inner protons (H3, H5) of me-β-CD can be observed due to the influence of the guest monomer. Similarly, the resonances of the atoms of the guest compound, which penetrate into the cavity are shifted, as well. It is interesting to note that the signals of the nine protons of the *tert*-butyl group are shifted most effectively to positive value compared to the other protons of the guest monomer. This strongly indicates a close host guest interaction of the spherical shaped *tert*-butyl




***Scheme 2.*** Equation of equilibrium of complexation for monomer (1).

group with the hydrophobic cavity. Only the proton *1a* is shifted to lower magnetic field, probably due to the influence of negatively charged oxygen atoms of the CD-ring being in a short distance of this proton *1a*.

The 2D-ROESY-NMR spectrum of the complexed monomer (Fig. 3) shows the following: the *tert*-butyl group is located deeply in the cyclodextrin torus. The protons of the *tert*-butyl group interact with all protons of me-β-CD, also with the inner protons H3 and H5, whereas the protons of the methyl-group interact preferably with the two methoxy-groups. The double bond is not located in the cyclodextrin torus. This means that the attack by radicals is easily achieved. Figure 4 elucidates the interactions of the *tert*-butyl group with the hydrophobic cavity. Due to the fact, that there are also crosspeaks between the *tert*-butyl group and the 2- and 6-methoxy group, we assume that the mobility of the guest monomer is high and, additionally, the equilibrium constant for the formation of (1a) should be relatively low.

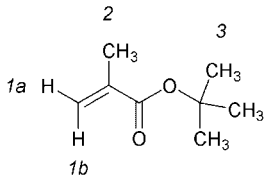
Using the Benesi–Hildebrand plot we thus calculated the host-guest binding constant K [$K = 65(\pm 4)\,M^{-1}$], which is a mean value of two different measurements.

***Table 1.*** $R_f$ values of the complex (1a) and the free monomer (1) in comparison with the $R_f$ value of me-β-CD (solvent methanol).

| | me-β-CD | 1 | 1a |
|---|---|---|---|
| $R_f$ | 0.61 | 0.92 | 0.54 |

***Table 2.*** Comparison of the $^1$H-NMR resonances of the uncomplexed monomer (1) and the complexed monomer (1a) in $D_2O$.

| | 1a | 1b | 2 | 3 |
|---|---|---|---|---|
| 1 | 6.00 | 5.60 | 1.85 | 1.47 |
| 1a | 5.90 | 5.69 | 1.87 | 1.60 |
| Δδ | −0.10 | +0.09 | +0.02 | +0.13 |




The absorbance values measured at different wavelengths gave the same equilibrium constant, which is an indication of a 1:1 stoichiometry of the complex. The parallelism of the lines in the Benesi–Hildebrand plot emphasizes the reliability of the measurements (Fig. 2). Now it is possible to calculate the concentration of complexed monomer $[M]_b$ and of free monomer [M] for the polymerization of *tert*-butyl methacrylate at 20°C with a total concentration $[M]_{tot}$ of $1.50 \cdot 10^{-1}$ M. Using the principle of mass action[24] we determined $[M]_b = 1.30 \cdot 10^{-1}$ M and $[M] = 2.03 \cdot 10^{-2}$ M. 14 mol% of the total monomer-concentration are not complexed at 20°C when we start the polymerization.

Table 3 summarizes the polymerization data. Polymer numbers signed with an additional b are synthesized in absence of me-β-CD. Polymerization of (1) at different temperatures (20°C and 80°C) was performed *via* complexation with me-β-CD and also, for comparison in absence of me-β-CD (signed with b). Two types of radical initiators

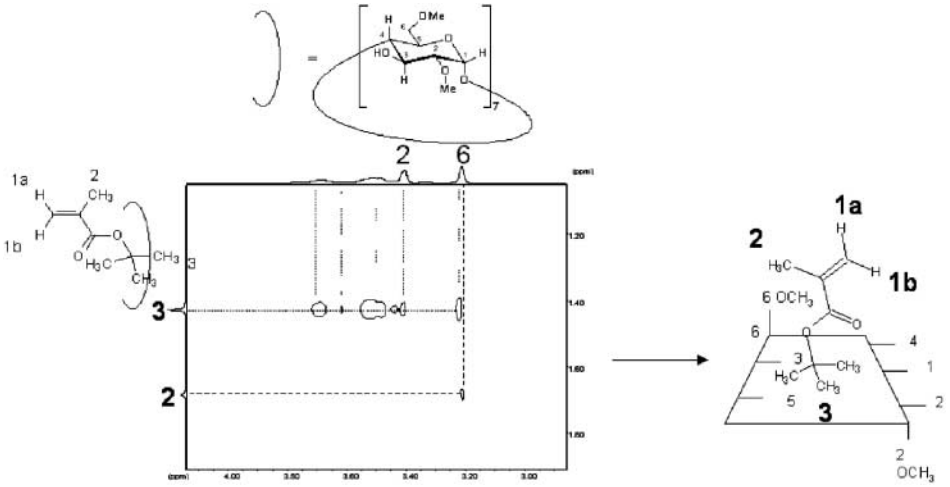



***Figure 3.*** 2D-ROESY-NMR spectrum of (1a) in $D_2O$.

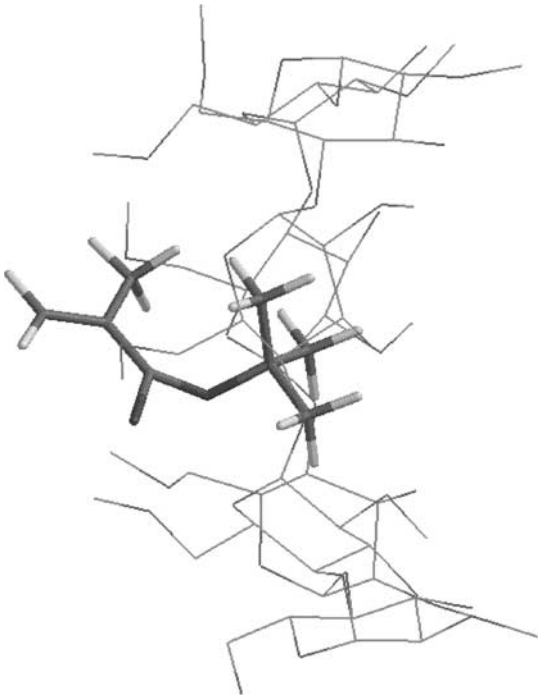


***Figure 4.*** Interactions between the *tert*-butyl group and the hydrophobic cavity of me-β-CD (geometry equilibration, PM3, SPARTAN).



were used: 2,2′-azobis(amidinopropane)-dihydrochloride (VA044) or potassium persulfate ($K_2S_2O_8$) in combination with sodium metabisulfite ($Na_2S_2O_5$).

The yields of run *2* and *3* do not differ significantly from each other (91% and 84%, respectively). However they are both significantly higher compared with the yields of

***Table 3.*** Results of polymerizations (polymers signed with an b are synthesized without me-β-CD).

| Run no. | Initiation system | Initiator (mol-%) | Temperature (°C) | Termination (min) | $M_w$ (g/mol) | $M_n$ (g/mol) | $M_w/M_n$ | Conversion (%) |
|---|---|---|---|---|---|---|---|---|
| 2 | VA044 | 5 | 80 | 40 | 30,900 | 15 300 | 2.02 | 91 |
| 2b | VA044 | 5 | 80 | 40 | 16,700 | 8 100 | 2.07 | 37 |
| 3 | $K_2S_2O_8$ | 1 | 80 | 40 | 23,300 | 12 100 | 1.92 | 84 |
| 3b | $K_2S_2O_8$ | 1 | 80 | 40 | 41,100 | 18 900 | 2.18 | 21 |
| 4 | $K_2S_2O_8$ | 1 | 20 | 90 | 38,600 | 19 700 | 1.95 | 72 |
| 4b | $K_2S_2O_8$ | 1 | 20 | 90 | [a] | [a] | [a] | [a] |
| 5 | $K_2S_2O_8$ | 1 | 20 | 40 | 64,100 | 27,200 | 2.36 | 76 |
| 5b | $K_2S_2O_8$ | 1 | 20 | 240 | [a] | [a] | [a] | [a] |

[a] No polymerization occurred.

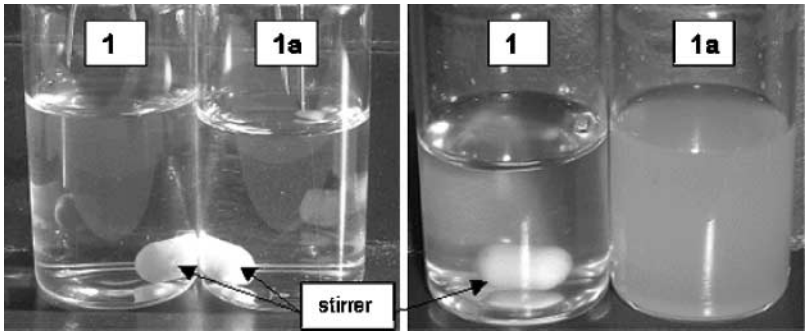



***Figure 5.*** Comparison of a polymerization at 20°C: left side: after initiation of polymerization; right side: after 5 min.

the polymerizations carried out without me-β-CD under similar conditions (Table 3, run *2b* and *3b*). The relatively low water solubility of the uncomplexed *tert*-butyl methacrylate (1) was determined at room temperature to $0.34 \pm 3\%$ g/L. This means that a very low monomer concentration in the aqueous phase is sufficient only for a relatively slow polymerization. As expected, no polymer was obtained from uncomplexed monomer in the presence of an initiator at room temperature.

Surprisingly, at room temperature (20°C) a rapid homopolymerization of the complex (1a) takes place. This strongly implies that the radicals preferently react with the complexed monomer (1a), and not with the low fraction of free uncomplexed monomer which is also present in the continuous aqueous phase. Figure 5 illustrates clearly the results of the polymerization-experiments obtained from (1a) and (1) at 20°C.

The effect of temperature on the polymerization of the complexed monomer is summarized in Sch. 1. The polymerization of the complexed monomer at room temperature proceeds through the dethreading of me-β-CD from the complex during chain propagation. The resulting polymer precipitates while me-β-CD remains in aqueous phase (path A). At high temperature polymerization also starts with the decomplexed monomer (path B). Under these conditions, the two pathways compete each other. In the experiments at 80°C (run *2*, *3*) we obtained relatively narrow unimodal molecular weight distribution (2.02 and 1.92). The prior complexation of the monomer before initiation seems to lead to a uniform grow of the chains and therefore to a low polydispersity.

By consideration of the above described results a polymerization at 20°C descends only from the complexed monomer (1a). At 80°C we have to consider two possible ways of polymerization due to the higher water solubility of (1) at elevated temperature.

## CONCLUSION

In this investigation we showed that 2,6-dimethyl-β-cyclodextrin enables the rapid polymerization of *tert*-butyl methacrylate in aqueous solution. At 20°C, no polymerization occurs without mediation of me-β-CD. It can be concluded that the radicals preferentially

react with the complexed monomer (1a), and not with the low fraction of free uncomplexed monomer (1) that is also present in the continuous aqueous phase.

## ACKNOWLEDGMENTS

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