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Kinetics of methyl methacrylate template polymerization.

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SUMMARY

A polymerization is called a template- or replica polymerization, if this polymerization is carried out in the presence of chain molecules of pre-formed polymer (the template) and proceeds along or in the proximity of those template molecules. Methyl methacrylate (MMA) as monomer and isotactic poly(methyl methacrylate) (PMMA) as template proved to be such template type polymerization. A better understanding of template polymerization could be gained from kinetic studies on the MMA/isotactic PMMA system.

Overall rates of template and analogous blank polymerization were determined by dilatometry. The influence of temperature, solvent type and the tacticity and molecular weight of the template on the polymerization process were investigated. An increase in the relative initial rate of template polymerization with respect to blank polymerization is observed at polymerization temperatures below 30°C (chapter 2). This rate increase is most pronounced at the lowest polymerization temperature with the highest molecular weight it-PMMA as a template in a strongly complexing solvent like dimethylformamide.

The overall activation parameters were calculated from the temperature dependence of the overall reaction rate constant. The activation energy as well as the activation entropy of the template polymerization showed a large decrease as compared to blank polymerization. These changes are ascribed to the stereoselection in the propagation step (lower activation entropy) and hindrance of segmental diffusion in the termination step (higher activation energy) of growing associated polymer radicals.

These suggestions were confirmed in chapter 3 by determination of the separate rate constants of propagation and termination. To this end the non-stationary sector technique was

applied besides stationary experiments under conditions favourable for template polymerization. It appeared that radical lifetime increases from 8.4 sec. for blank polymerization to 64 sec. for template polymerization. The calculated values of the rate constants for propagation (k_p) and termination (k_t) of template polymerization appeared to be about 5 times and 80 times lower than the corresponding values of blank polymerization, respectively.

The rate of initiation had to be determined in order to evaluate the rate constants k_p and k_t . In literature the rate of initiation is often determined by means of an inhibitor method, by which the dependence of inhibition period on inhibitor concentration is measured. This determination involves a neglect of the termination, which is not quite correct. Therefore, a detailed discussion of this subject is given in chapter 4.

In chapter 5 it appeared, that both initial polymerization rate and molecular weight of formed polymer depend strongly on template concentration. It was shown that the presence or absence of a homogeneous segmental distribution of template polymer in the reaction medium defines the mechanism of template polymerization. Below the critical concentration for a homogeneous segmental distribution template polymerization is restricted to a microphase containing one template chain. Above this critical concentration the growing chains can easily jump from one template molecule to another. So, the template polymerization proceeds along several template chains and a network is built up.

When template polymerization is continued at low temperatures to higher conversions, a second rate enhancement can take place in addition to the initial one (chapter 6). This phenomenon is also related to the complex formation between growing chain and template chain. This second template effect is probably caused by hindered translational motion of growing chains in a physical network, whereas the initial template effect was mainly ascribed to a hindered segmen-

tal motion of the chain radicals.

Finally, the general gel effect or Trommsdorff-Morrish effect is discussed in chapter 7. This effect appears at high conversions as a polymerization rate increase and is a rather general feature of vinyl radical polymerization. A comparison has been made of gel and template rate effects. It is suggested that the MMA gel effect is caused by formation of weak physical crosslinks. These crosslinks may arise from the association of short iso- and syndiotactic sequences in the growing chains with complementary sequences in already formed PMMA chains. The formation of these physical crosslinks results in a retarded termination and consequently in an enhancement of overall polymerization rate.