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 fa-
vourable for template polymerization. It appeared that rad-
cal lifetime increases from 2.4 sec. for blank polymerizati-
on to 64 sec. for template polymerization. The calculated
values of the rate constants for propagation \( k_p \) and ter-
mination \( k_t \) of template polymerization appeared to be a-
about 5 times and 80 times lower than the corresponding va-
lues 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 ra-
ette of initiation is often determined by means of an inhibi-
tor method, by which the dependence of inhibition period on
inhibitor concentration is measured. This determination in-
volves a neglect of the termination, which is not quite cor-
rect. Therefore, a detailed discussion of this subject is
given in chapter 4.

In chapter 5 it appeared, that both initial polymeriza-
tion 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 me-
chanism of template polymerization. Below the critical con-
centration for a homogeneous segmental distribution tem-
plate 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 tem-
peratures 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 be-
tween 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 ini-
tial template effect was mainly ascribed to a hindered segmen-
tual motion of the chain radicals.

Finally, the general gel effect or Zimm-Bragg 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 PMA 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 PMA chains. The formation of these physical crosslinks results in a retarded termination and consequently in an enhancement of overall polymerization rate.