Kinetics of methyl methacrylate template polymerization.

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SUMMARY

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

Overall rates of template and analogous blank polymeri-
zation were determined by dilatometry. The influence of tem-
perature, solvent type and the tacticity and molecular weight
of the template on the polymerization process were investiga-
ted. An increase in the relative initial rate of template po-
lymerization with respect to blank polymerization is obser-
ved at polymerization temperatures below $30^{\circ}C$ (chapter 2).
This rate increase is most pronounced at the lowest polyme-
rization temperature with the highest molecular weight it-PMMA
as a template in a strongly complexing solvent like dimethyl-
formamide.

The overall activation parameters were calculated from
the temperature dependence of the overall reaction rate con-
stant. The activation energy as well as the activation entro-
py 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 activa-
tion entropy) and hindrance of segmental diffusion in the ter-
mination step (higher activation energy) of growing associ-
ated polymer radicals.

These suggestions were confirmed in chapter 3 by determi-
nation of the separate rate constants of propagation and ter-
mination. 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 0.4 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-Norrish
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 forma-
tion of weak physical crosslinks. These crosslinks may arise
from the association of short iso- and syndiotactic sequen-
ces in the growing chains with complementary sequences in
already formed PMMA chains. The formation of these physical
crosslinks results in a retarded termination and consequent-
ly in an enhancement of overall polymerization rate.

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