

Characterization of the photopolymerization - kinetics of inorganic-organic nanocomposite materials by Photo-DSC

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1. Introduction

Organic-inorganic sol-gel derived composites with poly(methylmethacrylate) chains formed by polymerization already have shown their usefulness for many optical applications including embossing and holography technics to produce aspherical lenses, optical lattices and coatings for optical fibers^{1,2,3}. They can combine relatively low shrinkage with efficient photopolymerization and show overall properties being superior to those of pure methacrylate based polymers. The investigation of the kinetics of the radical polymerization however of methacrylate precursors containing hydrolyzable alkoxy silane groupings in sol-gel composite materials is more difficult due to the high inorganic crosslinking and the resulting high insolubility. For these reasons, Photo-DSC^{4,5} was assumed to be a useful method to investigate the kinetics of precursor systems, together with appropriate photoinitiators. The purpose of this work is to investigate the influence of the inorganic network formation on the kinetics of free radical polymerization reaction in methacryloxypropyltrimethoxysilane (MPTS) systems.

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2. Experimental

Photo-DSC was used to monitor the organic network formation in MPTS systems which were prehydrolyzed with different amounts of diluted (5mmole/l) HCl. Irgacure 184 (Ciba - Geigy) was used as photoinitiator (concentration ratio 2,5 mole % on the basis of the methacrylate end-groups equal to 100%). The heat flow of the polymerizing system was used as a measure for the degree of conversion. The conversion rate was controlled by analyzing the double bond content in the polymerized systems. $^{29}\text{Si-NMR}$ was used to monitor the inorganic network formation^{6,7,8}. The amounts of T^0 species as calculated from the $^{29}\text{Si-NMR}$ spectra were used to monitor the kinetic of the hydrolysis and condensation reaction.

3. Results and Discussion

As method for the investigation of the hydrolysis and condensation reaction in MPTS systematically $^{29}\text{Si-NMR}$ spectroscopy was chosen. Figure 1 shows the $^{29}\text{Si-NMR}$ spectra of MPTS hydrolyzed with 5mmole/l HCl in the molar ratio 1/2 accumulated at different times. The data obtained from integration of the $^{29}\text{Si-NMR}$ spectra of these experiments are shown in figure 2. As can be seen from figure 1 the T^0 species from unhydrolyzed MPTS are still present until 2h after adding HCl. While T^0 is decreasing relatively fast the T^0_x species concentration reaches a maximum value. As one can also see, the reaction rate for hydrolysis and condensation in this system is rather fast and there are only few T^0 and T^0_x silanol species after 2h reaction time.

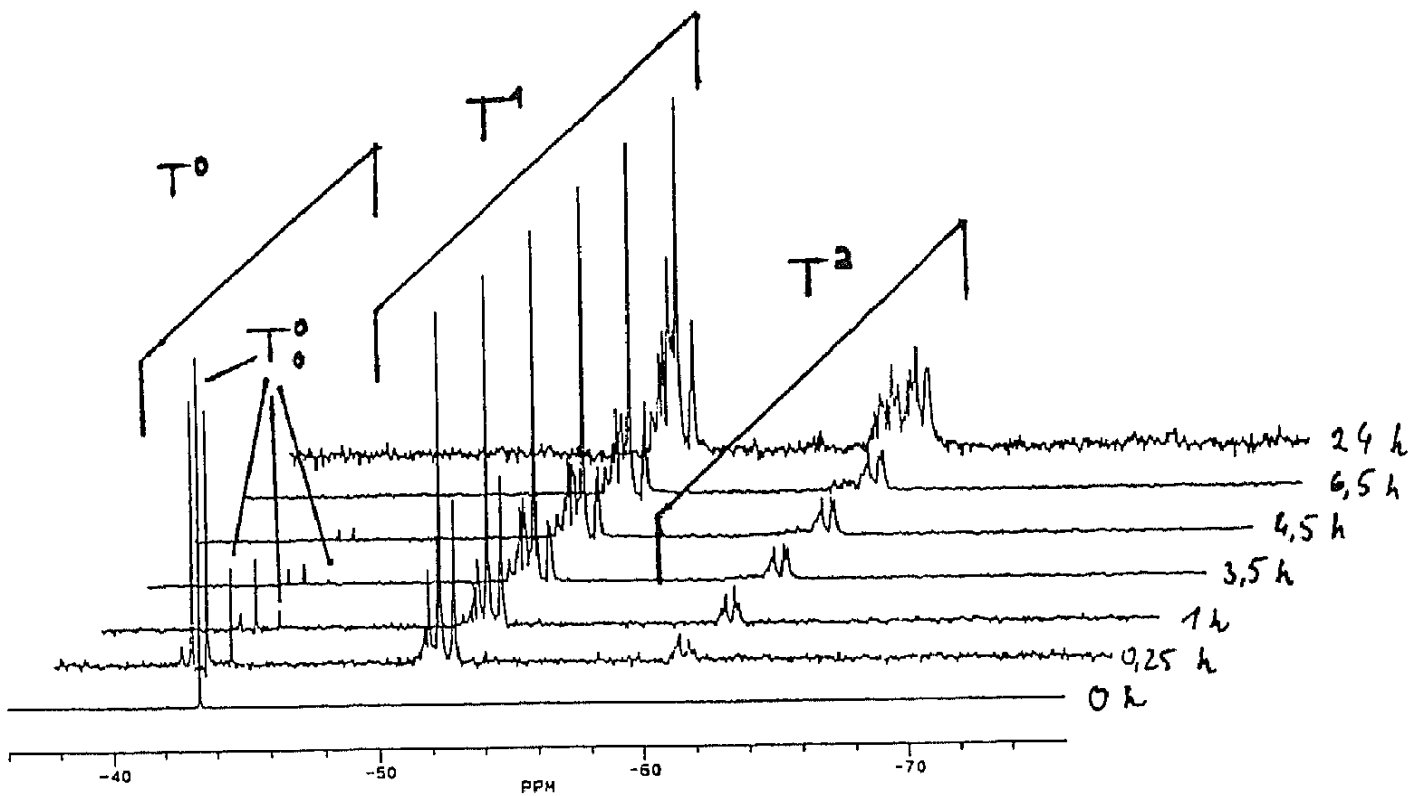


Figure 1: ^{29}Si -NMR spectra of MPTS, prehydrolyzed with 5mmole/l HCl molar ratio 1/2 accumulated at different times after adding HCl. ^{29}Si -NMR spectrum at $t = 0$ represents unhydrolyzed MPTS

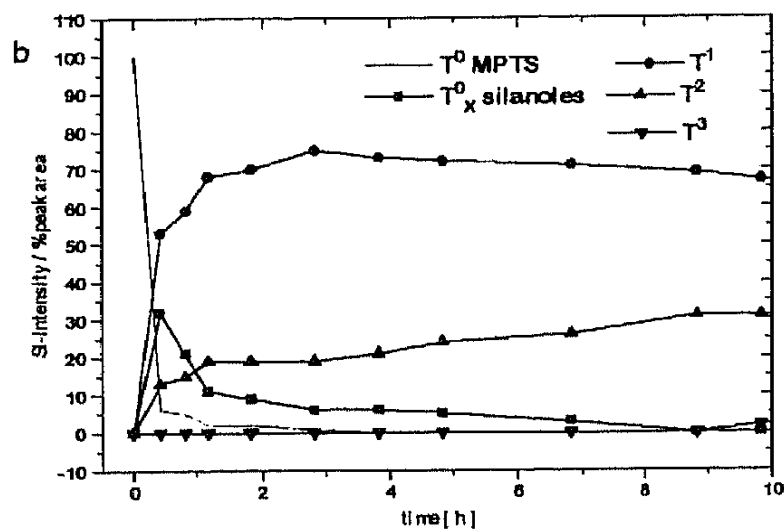


Figure 2: Time - dependent ^{29}Si -NMR documentation of hydrolysis and condensation reaction of MPTS prehydrolyzed with 5mmole/l HCl at room temperature (molar ratio 1/2)

The investigation of the polymerization kinetics after 1h, 6h and 24h showed that there are only slight differences between the different hydrolysis times, but large differences to the unhydrolyzed MPTS (figure 3).

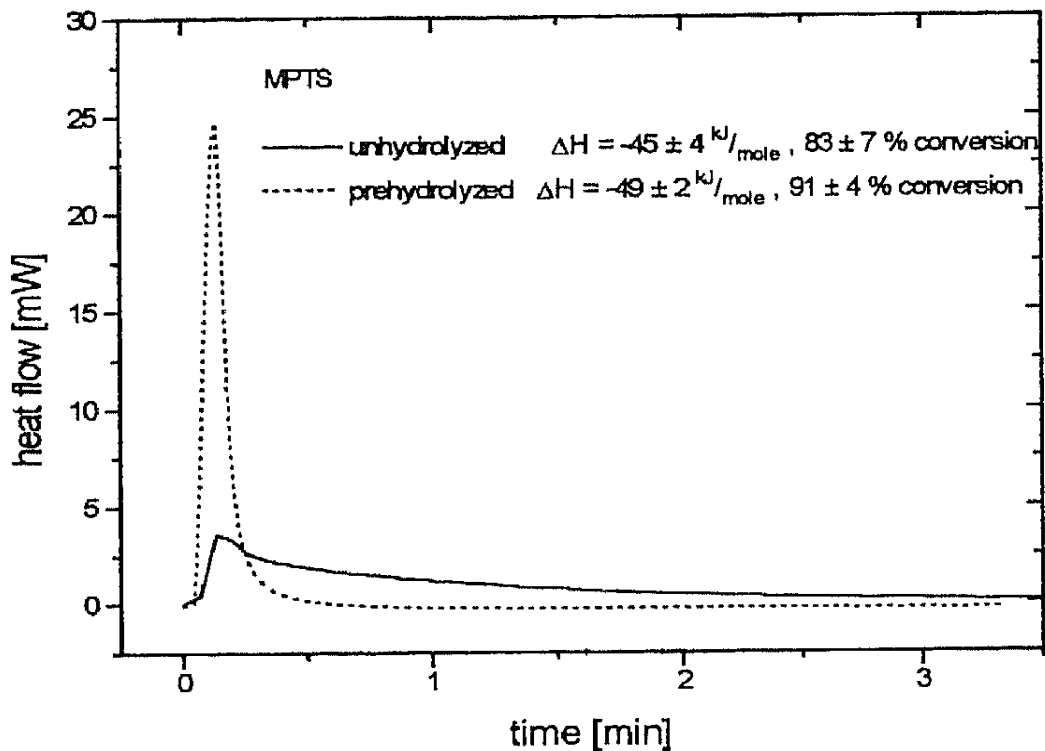


Figure 3: Time dependence of the heat flow during photopolymerization of MPTS

- MPTS unhydrolyzed, photoinitiator Irgacure 184 (2,3 mole %)
- MPTS prehydrolyzed with 0,1 mol/l HCl , photoinitiator Irgacure 184 (2,5 mole %), 6h after adding HCl

As one can see from figure 3, the polymerization rate of the hydrolyzed species is remarkably higher than that of the unhydrolyzed ones.

For a better discrimination of the influence of the state of hydrolysation on the kinetics it seemed to be advantageous to use reaction parameters known to slow down the reaction rate. For this reason and in order to obtain data about the influence of the T^0 species, the H_2O/HCl concentration was decreased. Figure 4 shows therefore the ^{29}Si -NMR spectra of MPTS prehydrolyzed with 5mmole/l HCl in the molar ratios $\equiv SiOR:H_2O/HCl$ 1/4 and 1/20 90min after adding the H_2O/HCl .

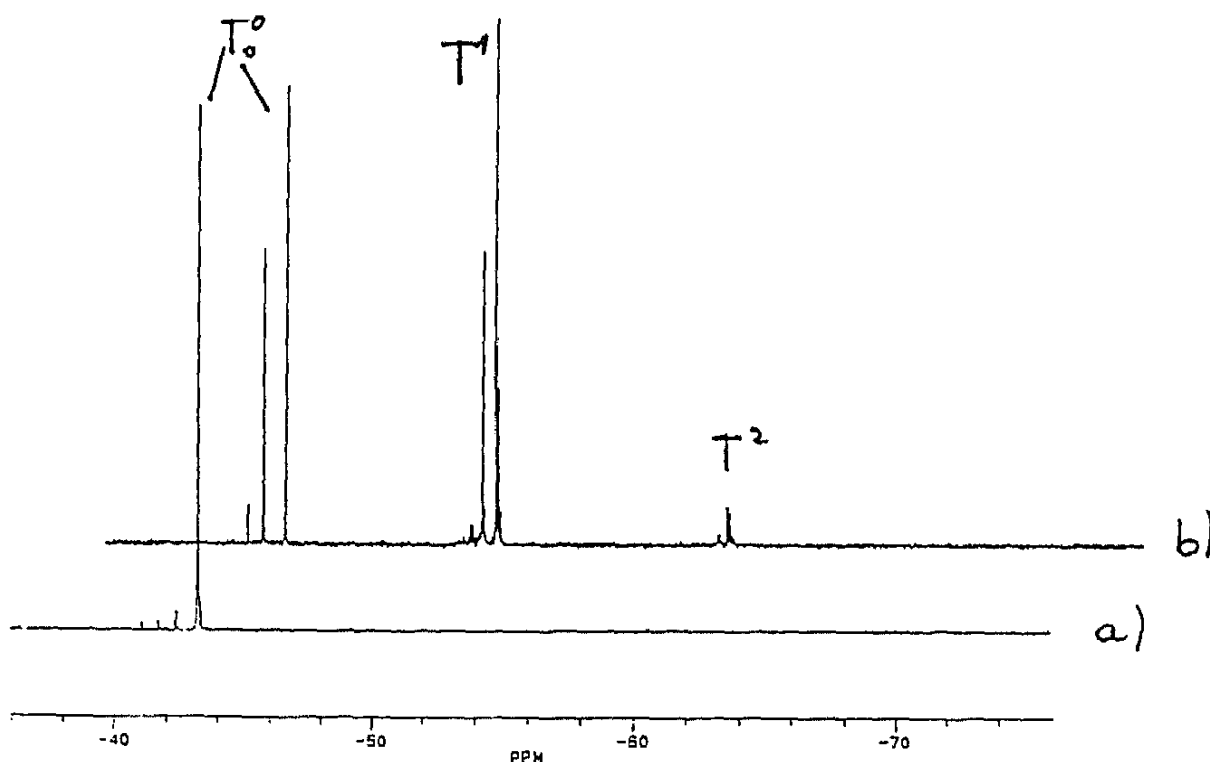


Figure 4: ^{29}Si - NMR spectra of MPTS prehydrolyzed with 5mmole/l HCl 90min after adding the acid
 a) prehydrolyzed with the molar ratio 1/20
 b) prehydrolyzed with the molar ratio 1/4

It is evident from figure 4 that the hydrolysis and condensation reaction is much slower in the case of molar ratio 1/4 and 1/20 respectively than in

the case of molar ratio 1/2. Figure 5 shows the Photo-DSC curves of the three systems MPTS prehydrolyzed with 5mmol/l HCl in the molar ratios $\equiv\text{SiOR}:\text{H}_2\text{O}/\text{HCl}$ 1/2, 1/4 and 1/20 compared to unhydrolyzed MPTS.

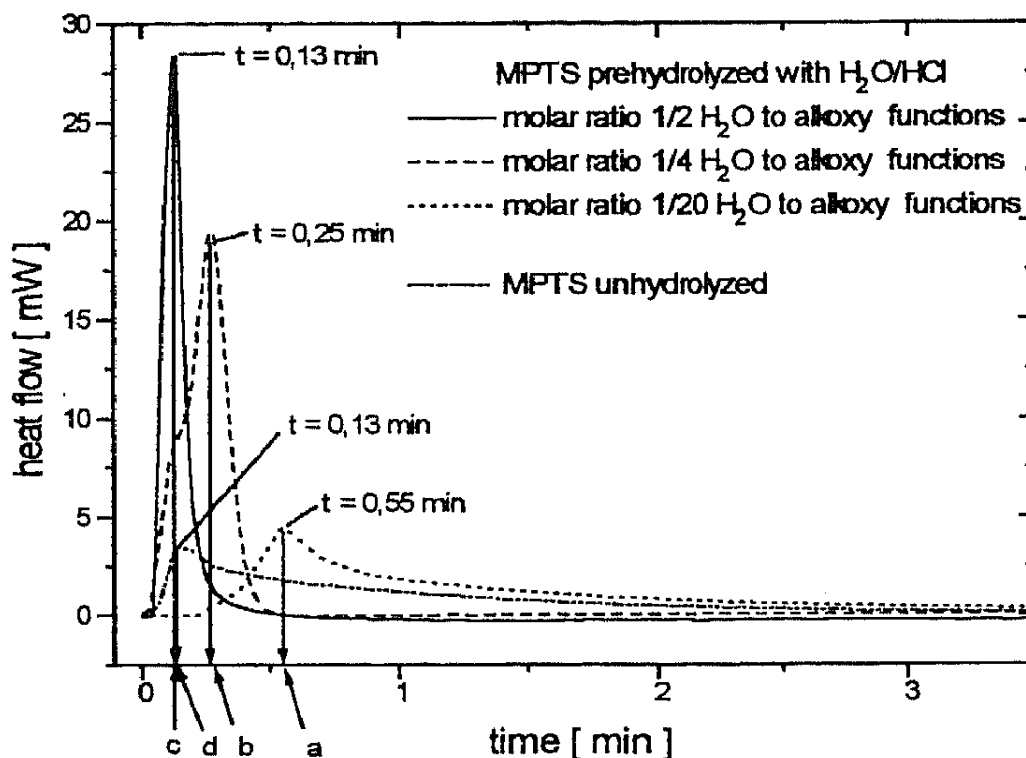


Figure 5: Time dependence of the heat flow during photopolymerization of MPTS (prehydrolyzed with 5mmol/l HCl at room - temperature, solvent containing system) 90min after adding the acid, photoinitiator Irgacure 184, peak maxima of:
a: molar ratio 1/20 (initiator concentration 2,4 mole%)
b: molar ratio 1/4 (initiator concentration 2,5 mole%)
c: molar ratio 1/2 (initiator concentration 2,5 mole%)
d: MPTS unhydrolyzed (initiator concentration 2,3 mole%)

From the DSC curves the ΔH values can be calculated and using literature data for the ΔH values for the conversion of methacrylate double bonds, the conversion rates of the different systems were evaluated. Table 1 summarizes all the results of the Photo-DSC and ^{29}Si -NMR measurements.

Table 1: Calculated enthalpies (ΔH_n) and calculated conversion rates of MPTS (prehydrolyzed with 5mmol/l HCl at room temperature, 90min after adding the acid, solvent containing system) for different molar ratios of hydrolysis; T^0_0 and T^0_x concentrations ($x=1,2,3$) and T^1 , T^2 and T^3 concentrations and the calculated amounts of generated methanol in mol/mol MPTS

hydro-lysis	T^0_0	T^0_x	T^1	T^2	T^3	ΔH_n	MeOH concentr.	con-vers.	peak max.
ratio	mole %	mole %	mole %	mole %	mole %	kJ/mole	mole/mole MPTS	%	t (min)
1/2	2	9	60	27	2	49,5	2,95	89	0,13
1/4	17	16	58	9	0	47,0	0,55	86	0,25
1/20	92	8	0	0	0	50,6	0,25	89	0,55
MPTS	100	0	0	0	0	45,0	0	83	0,13

As we can see from table 1 the conversion rate is not dependent on the amount of T^0_0 species in the reaction mixture. But as we can see from figure 4 and table 1 together the time to reach maximum heat flow in the

system increases with increasing T^0_0 and T^0_x content. This means that the kinetic is influenced remarkably by the degree of hydrolyzation and condensation. The kinetic becomes faster with increasing degree of hydrolyzation and condensation and even in the ratio 1/2 experiment, where considerable amounts of condensed species with higher molecular weights are present, the kinetics are increased. This means, that the diffusion of the system is not the rate limiting step under the experimental conditions, but more likely the SiOR groupings seem to play an inhibiting effect on the radical polymerization in these systems.

4. Conclusion

The experiments have shown that in organoalkoxysilanes like MPTS high degrees of conversions can be obtained despite polycondensation process occurring at the same time like the photopolymerization. This is important for using MPTS as a precursor for sol-gel composite materials if the methacrylate grouping is used for building up PMMA chains.

5. References

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