Copolymerisation of Maleic Anhydride with Electron-Acceptor Monomers

*Jens Ferbitz, Werner Mormann**

Universität Siegen, Fachbereich 8, Laboratorium für Makromolekulare Chemie, Adolf-Reichwein Str. 2, 57068 Siegen, Germany

Summary: Copolymerisation of maleic anhydride with *tert.*-butyl methacrylate and trimethylsilyl methacrylate was studied. Both monomers form random copolymers with maleic anhydride and in both cases the acceptor monomer is incorporated preferentially into the copolymer. Maleic anhydride which does not homopolymerise has reactivity ratios of approximately zero. The esters have reactivity ratios of 12.8 for trimethylsilyl methacrylate and 2.95 for *tert.*-butyl methacrylate. Thermal behavior and molar masses were investigated as a function of composition. Conditions for hydrolysis of the trimethylsilyl ester groups to give free acid groups have been established.

Introduction

Maleic anhydride is one of the best studied electron-acceptor monomers. It can not be homopolymerised under normal conditions[1] but it is often used for grafting and especially for alternating copolymerisation with electron-donor monomers.[2] In a previous study on copolymerisation of multifunctional monomers we investigated the alternating copolymerisation of maleic anhydride with 2-isopropenyl isocyanate.[3] We also described the copolymerisation of the latter with trimethylsilyl methacrylate, a typical electron-acceptor monomer.[4] So far little is known about the copolymerisation of maleic anhydride with electron-acceptor monomers like methacrylic acid esters. Two monomers of this kind are *tert.*-butyl methacrylate and trimethylsilyl methacrylate. Homopolymerisation of both esters has been reported,[5,6] block copolymers and random copolymers of the *tert.*-butyl ester are known as well.[7,8] But nothing is known about their copolymerisation with maleic anhydride.

This is quite remarkable as the resulting copolymers are widely used, for example in microlithographic applications. Photoresist polymers for 193 nm microlithography often contain maleic anhydride to stiffen the chain and thus rise glass transition temperature or to use it for further reactions like wet silylation.[9] Trimethylsilyl methacrylate improves dry-etch-resistance[10] and *tert.*-butyl methacrylate is commonly used as acid labile protection group.

Therefore, we focused on the copolymerisation of *tert.*-butyl methacrylate with maleic

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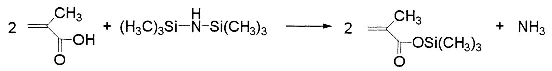
anhydride and compared it to the copolymerisation of the anhydride with trimethylsilyl methacrylate, a monomer with the same steric requirements but a different electron density of the double bond. Due to the pπ - dπ interaction of the ester oxygen with the silicon a decreased electron density of the double bond can be expected. The obtained copolymers should show different properties due to their functional groups. The *tert.*-butyl methacrylate copolymers have a thermal labile group while the trimethylsilyl ester group can be easily cleaved by hydrolysis using even weak acids. Both the thermal and the hydrolytic reaction give methacrylic acid. The reactivity ratios obtained by our studies can be used as an important tool to design copolymers for photoresist applications.

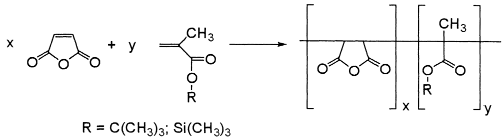
In this communication we describe the free radical copolymerisation of maleic anhydride **1** with *tert.*-butyl methacrylate and **2** trimethylsilyl methacrylate **3**.

Results and discussion

Trimethylsilyl methacrylate was synthesized according to the method described by Chapman and Jenkins[11]:



For copolymerisation solutions of the monomers in 2-butanone were prepared and 1 mol-% α,α-azodiisobutyronitrile was used as initiator:



The obtained polymers were precipitated in proper nonsolvents in case of the *tert.*-butyl ester copolymers or isolated by repeated freeze-drying from dry benzene in case of the trimethylsilyl ester copolymers. The experiments are summarized in Table 1 and 2. Conversion was tried to be kept below 20%. The composition of the copolymers from maleic anhydride and trimethylsilyl methacrylate was calculated from nuclear magnetic resonance (NMR) spectra using the area of the resonance of the trimethylsilyl group at around 0 ppm and the sum of the areas of the other resonances. The composition of the copolymers from *tert.*-butyl methacrylate and maleic anhydride was calculated from thermal gravimetry (TGA). This method was applied as the integration from the ^{1}H-NMR-spectra was not possible due to small resonances of anhydride protons and overlapping of all signals (Figure 1). The results were compared to results obtained by elemental analysis and invers-gated ^{13}C-NMR-spectra. A good agreement was found with errors in the range of integration errors in nuclear magnetic resonance spectroscopy (about 5%).

Table 1. Copolymerisation (60 °C) of maleic anhydride **1** and *tert.*-butyl methacrylate **2**.

No.	$f_{\text{anhydride}}$ feed	Yield / %	$F_{\text{anhydride}}$ polymer$^{a)}$	Elemental analysis found (calc.) / %		TGA onset / °C	DSC Peak ΔH / J·g^{-1}	M_n / 10^4 g mol^{-1} (D)
				H	C			
4	0.529	19.5	0.226			194	177 416 endo	5.88 (1.89)
5	0.636	15.0	0.268	8.84 (8.59)	63.24 (63.15)	188	162 438 endo	5.25 (1.55)
6	0.728	21.6	0.340			180	154 432 endo	1.84 (2.48)
7	0.788	18.9	0.345			172	125 394 endo	1.16 (2.20)
8	0.876	18.2	0.416	7.31 (6.47)	59.22 (59.43)	166	125 215 endo	1.51 (1.91)
9	0.931	12.9	0.406			162	123 209 endo	2.37 (2.79)

Table 2. Copolymerisation of maleic anhydride **1** and trimethylsilyl methacrylate **3**.

No.	$f_{\text{anhydride}}$ feed	T / °C	Yield / %	$F_{\text{anhydride}}$ polymer$^{a)}$	M_n / 10^5 g mol^{-1} (D)
10	0.923	70	15	0.471	4.57 (3.73)
11	0.910	70	15	0.424	1.58 (2.84)
12	0.900	70	15	0.403	1.59 (3.69)
13	0.856	60	15	0.315	-
14	0.797	60	15	0.223	3.73 (1.90)

a) calculated from ^{1}H-NMR

Figure 1 and 2 show the NMR-spectra of the polymers. In case of the *tert.*-butyl methacrylate copolymers the signal of the *tert.*-butyl protons can be found at 1.4 ppm, overlapping with the signal of the methylene protons at lower field and that of the other methyl protons at higher field. Between 2.8 and 3.4 ppm a very broad signal is due to the resonance of the maleic anhydride protons.

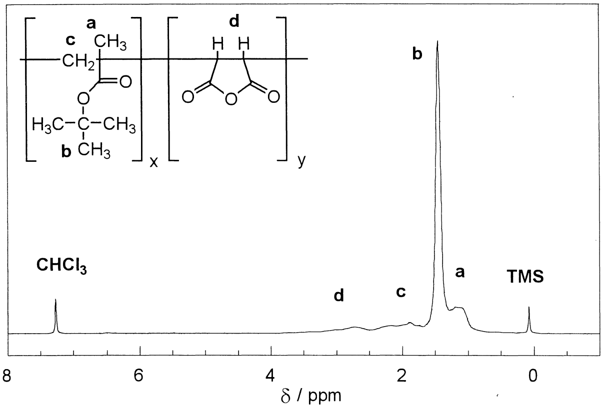


Figure 1. NMR-spectrum (200 MHz) of poly(*tert.*-butyl methacrylate-co-maleic anhydride).

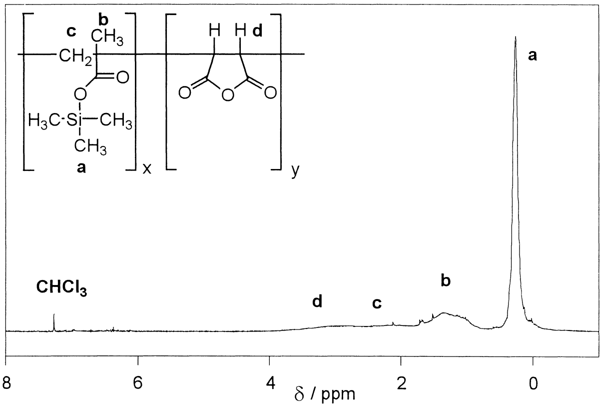


Figure 2. NMR-spectrum (200 MHz) of poly(maleic anhydride-co-trimethylsilyl methacrylate).

The spectra of trimethylsilyl ester polymers show the same signals for methylene, maleic anhydride and methyl protons. But the signal of the trimethylsilyl group is shifted to about 0 ppm because of the different electronic influence of silicon center atom compared to the carbon center atom.

The IR-spectrum of a *tert.*-butyl methacrylate (Figure 3) copolymer shows significant signals at 2978 (C-H), 1860, 1786 (C=O and C-O-C of maleic anhydride) and 1720 cm^{-1} (C=O *tert.*-butyl methacrylate).

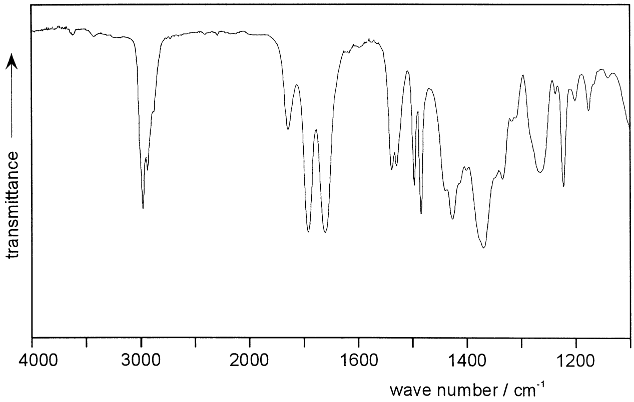


Figure 3. IR-spectrum of poly(*tert.*-butyl methacrylate-co-maleic anhydride).

As the conversion in all copolymerisations is higher than 10% we used the extended Kelen-Tüdős method[12] to calculate the reactivity ratios (Figure 4). The values obtained were compared to values given by a non-linear-least-square-method (NLLS).[13] The data are summarized in Table 3. They clearly show that in both cases an "ideal" non-azeotropic behavior (Figure 5) in the copolymerisations is observed.

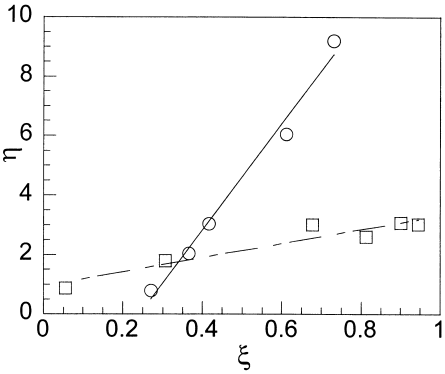


Figure 4. Kelen-Tüdős plots (□ **2**, ○ **3**).

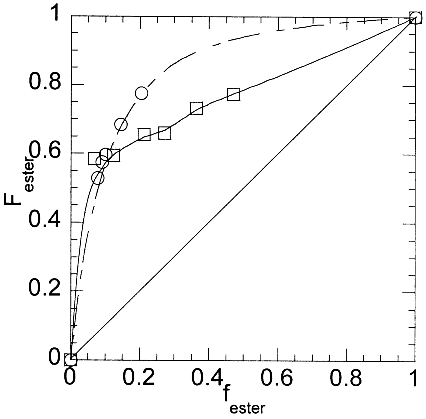


Figure 5. Copolymerisation plots (□ **2**, ○ **3**).

In both cases random copolymers are formed with the ester comonomer far preferentially incorporated into the growing chain. The values given by the two different methods are in good agreement and have acceptable errors. The reasons for remarkable errors in this study are on the one hand the reactivity ratio of the anhydride close to zero and on the other hand the great difference in r_1 and r_2. In one case even a negative reactivity ratio for the anhydride was calculated which is of course not possible and caused by small errors shifting the value from small positive to small negative figures. The reactivity ratios show that the trimethylsilyl methacrylate is more reactive towards the radical chain end than the *tert.*-butyl methacrylate. This can be seen in copolymerisation diagram and the Kelen-Tüdős plot as well. This results are confirmed by the copolymerisation of both esters where the trimethylsilyl ester is incorporated preferentially into the polymer as well.[14]

Table 3. Reactivity ratios obtained by different methods.

Monomer	Reactivity ratios	
	Kelen-Tüdős	NLLS
Trimethylsilyl methacrylate	13.61 ± 2.21	12,80 ± 0.99
Maleic anhydride	0.02 ± 0.01	0,07 ± 0.01
tert.-Butyl methacrylate	3.14 ± 0.27	2.95 ± 0.28
Maleic anhydride	-0.008 ± 0.004	0 ± 0.010
tert.-Butyl methacrylate	0.154 ± 0.043	0.180 ± 0.050
Trimethylsilyl methacrylate	1.367 ± 0.131	1.200 ± 0.229

As it is difficult to analyze the composition of the copolymers by means of NMR-spectroscopy we tried to establish another spectroscopic method to calculate the anhydride content in polymers containing *tert.*-butyl methacrylate and maleic anhydride. To solve this problem we tried to find an integration method using IR-spectra to determine the composition.

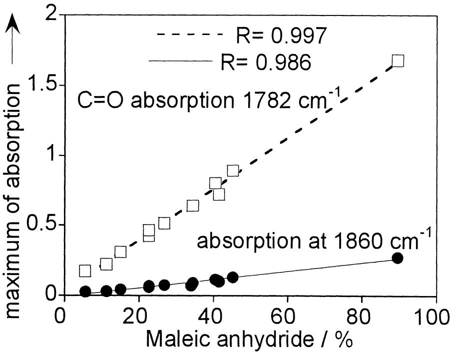
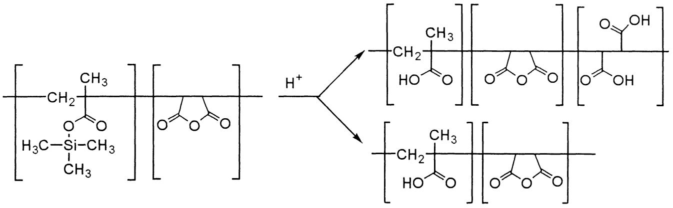


Figure 6. Calculation of maleic anhydride content from IR-spectroscopy.

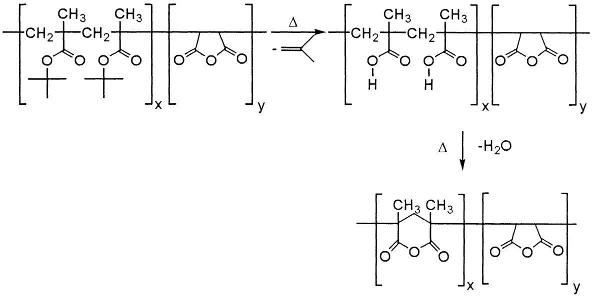
We prepared solutions of copolymers with different anhydride content in chloroform. The concentration of all solutions was the same and so we were able to make a calibration by simply plotting the maximum of absorption of the peaks at 1782 and 1860 cm^{-1} versus anhydride content in polymer (Figure 6). Both plots are straight lines and thus it is possible to calculate the anhydride content from the obtained linear fits. As the absorption at 1782 cm^{-1} is much stronger than that at 1860 cm^{-1} the error using this peak for integration is smaller than using the peak at 1860 cm^{-1}.

The copolymers of the esters with maleic anhydride have two different reactive groups apart from the anhydride group. The trimethylsilyl methacrylate group can be hydrolyzed by acids[6] and the *tert.*-butyl methacrylate group cleaved thermally both yielding methacrylic acid groups. The problem we faced was that the maleic anhydride content was not unaffected by hydrolysis using stronger acids (Scheme 1). Even the use of water or methanol does not prevent cleavage of the maleic anhydride groups. Isopropanol finally was found to be a proper alcohol to hydrolyze the ester but remaining the anhydride content constant.



Scheme 1. Hydrolysis of trimethylsilyl methacrylate containing copolymers.

The thermal behavior of copolymers containing *tert.*-butyl methacrylate and maleic anhydride is described in scheme 2.



Scheme 2. Thermal behavior of *tert.*-butyl methacrylate containing copolymers.

In a first step the ester groups are cleaved yielding isobutene and methacrylic acid groups. In a further step neighbored acid groups form six-membered anhydride rings under evaporation of water as side-product. In a poly(methacrylic acid) 86.5% of the acid groups statistically form anhydride groups. We studied the thermal behavior of our copolymers by differential scanning calorimetry (DSC) and thermal gravimetry. Typical diagrams obtained are shown in figure 7. In DSC we observed a strong endotherme with peak temperature of 123 to 177°C depending on polymer composition. With rising ester content of the copolymer the enthalpy of the endotherme rises as this signal is due to the ester cleavage and formation of anhydride. In some cases it can be distinguished between ester cleavage and anhydride formation as two peaks are found but in most cases both reactions can not be separated. The peak temperature of the found signal increases with decreasing anhydride content of the copolymer. This can be due to a small amount of acid formed in the copolymer during handling or reaction catalyzing the ester cleavage. The same relationship can be found in TGA looking at the onset temperatures of the observed weight loss.

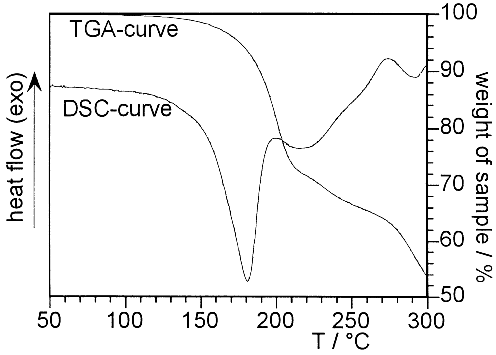


Figure 7. Thermal behavior of copolymer **4.**

Glass transition temperatures of the polymers could not be determined as they are in the temperature region where ester cleavage takes place.

Conclusions

Copolymerisation of maleic anhydride with *tert.*-butyl methacrylate and trimethylsilyl methacrylate were studied and the reactivity ratios were found to be $r_{tert.\text{-butyl methacrylate}} = 2.95$ / $r_{\text{maleic anhydride}} = 0.01$ and $r_{\text{trimethylsilyl methacrylate}} = 12.8$ / $r_{\text{maleic anhydride}} = 0.01$. A linear relationship was established that enables the determination of copolymer composition from

IR-spectra. It could be found that the temperature for the *tert.*-butyl ester cleavage increases with increasing ester content of the polymer. It could although been shown that hydrolysis of the trimethylsilyl ester with isopropanol does not effect the maleic anhydride content of the copolymer while methanol, water and even stronger protic solvents cause ring opening reactions. The presented results enable us to design copolymers with a given composition, reproducible content of each monomer and properties. This is a valuable tool in resist design and fabrication.

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