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Copolymers from *tert*-butyl methacrylate and itaconic anhydride—reactivity ratios and polymer analogous reactions

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Abstract

Free radical copolymerisation of *tert*-butyl methacrylate (**1**) and itaconic anhydride (**2**) has been investigated and reactivity ratios $r_1 = 0.272 \pm 0.08$ and $r_2 = 0.301 \pm 0.09$ have been obtained. Peak temperature of the endotherm and the enthalpy of the *cis*-elimination of the *tert*-butyl ester show a linear dependence on the content of anhydride in the copolymer. Alcoholysis of the anhydride with methanol resulted in complete formation of monomethyl itaconate, whereas the reaction with isopropanol in the presence of *N*,*N*-dimethyl-aminopyridine as catalyst stopped at lower conversion. Re-formation of the anhydride takes place around 100 °C in case of the monoisopropyl itaconate and at 120 °C for the monomethyl ester. This offers the possibility to adjust polymer properties, e.g. glass transition temperatures and solubility by controlled polymer analogous reaction. The copolymers can be used in photoresist processing, where adhesion and solubility can be adjusted during processing by alcoholysis and baking steps.

1. Introduction

Photoresist materials for application in 193 nm microlithography mostly contain the *tert*-butyl ester moiety as acid labile protection group (*tert*-butyl methacrylate) and often an anhydride structure from maleic anhydride to increase the glass transition temperature and as reactive group [1–9].

The anhydride structural element can serve various purposes. Alcoholysis can introduce acid groups which are useful to increase polarity and thus adhesion properties of the resist [10]. The anhydride can react with suitable amino groups bearing polymers to increase the thickness of the resist layer [8]. This reaction is used in the so called CARL-process (CARL, chemically amplification of resist lines) [11–14]. This process uses a bottom resist and a top-resist, in which the image is formed. A photo-acid generator forms an acid upon irradiation with UV-light of suitable wavelength. This acid catalyses *cis*-elimination of isobutylene from the *tert*-butyl ester groups giving acid groups which make the irradiated parts soluble in alkaline aqueous media. Before plasma-etching the remaining structure is cross-linked by reaction, e.g. of anhydride moieties, with α,ω-aminopropyl-oligo-siloxane. The siloxane gives a protective layer of SiO_2 in the oxygen plasma. Important amounts of anhydride in the polymer are often required for these applications. As maleic anhydride does not homopolymerise under normal conditions of free radical polymerisation the maximum mol fraction is 0.5 in alternating copolymerisation with electron releasing comonomers. With electron deficient comonomers like *tert*-butyl methacrylate a large excess of maleic anhydride is required for incorporation of reasonable amounts in the copolymer. This, however, creates difficulties in isolation and purification of the polymers.

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A monomer which could replace maleic anhydride is itaconic anhydride [15]. Itaconic acid anhydride can be homopolymerised by free radical polymerisation and can undergo all the reactions of maleic anhydride in microlithography. An advantage is that this monomer has not to be used in large excess if higher mol fractions of anhydride are required. Furthermore a more homogeneous random distribution along the chain is to be expected. Reactivity ratios of itaconic anhydride with *tert*-butyl methacrylate have not been described in the literature up to now.

Monoalkyl itaconates symmetric and non-symmetric dialkyl itaconates have been used for the synthesis of polymers with interesting physical properties [16–18]. Thus glass transition temperature T_g of the copolymers and hydrophilic/hydrophobic properties can be adjusted [19]. The copolymers have properties between those of the brittle poly(monoalkyl itaconate)s and the poly-(dialkyl itaconate)s [20]. Results on block copolymers of monobutyl itaconate and monocyclohexyl itaconate have been published by Cvetkovska et al. [21]. Interestingly enough polymer analogous modification of poly(itaconic anhydride) or its copolymers has not been reported in the literature to date. Controlled partial alcoholysis or hydrolysis would be a further convenient method to adjust properties of the resist polymer.

The present paper reports on the copolymerisation of itaconic anhydride and *tert*-butyl methacrylate and polymer analogous reactions of these copolymers with respect of to applications in photoresists.

2. Experimental part

Methods of characterization: IR-spectra were recorded on a Bruker Equinox 55 FTIR spectrometer, ^{1}H/^{13}C-NMR-spectra (Bruker AC-400) were obtained in deuterochloroform or dimethylsulfoxide-d_6 with tetramethylsilan or dimethylsulfoxide as internal standard. Thermal properties were determined on a Mettler TC 11/15 system with DSC 30 and TG 50 equipment. Size exclusion chromatography was performed with a PSS-system 2000, consisting of a UV-detector Lambda 1010, a RI-detector Shodex RI71; eluent: THF; columns: 3 PSS-SDV/5 gel-columns (7.8 × 300 mm; 5 μm particle size; 10^3, 10^5, 10^6 Å pore radius); calibration: polystyrene standards.

Materials: tert-Butyl methacrylate (TCI, Japan) was purified by distillation over calcium hydride in vacuo before use. Itaconic acid anhydride (Aldrich) was freshly distilled in a Kugelrohr apparatus (Büchi) prior to use. Azodiisobutyronitrile (AIBN) was recrystallized from diethyl ether. Solvents used were dried according to literature procedures. All reactions were made in flame dried glass equipment in an atmosphere of dry argon.

2.1. Synthesis of copolymers for reactivity ratios (general procedure)

In a 25 ml flame dried nitrogen flask itaconic acid anhydride and *tert*-butyl methacrylate were dissolved in 2-butanone to give a 50 wt.% solution. 0.01 mol% AIBN referring to the total amount of monomers was added. The mixture was degassed in three freeze-and-thaw cycles, and polymerised in an oil bath at 60 °C. Polymerisation was stopped by cooling to −20 °C. The polymers were isolated by precipitating from the tenfold amount of cyclohexane and thermostating at 70 °C in vacuo to remove residual volatiles.

2.1.1. Copolymers for alcoholysis

Polymerisation with continuous feed of itaconic anhydride: In a 500 ml flame dried three-necked nitrogen flask equipped with magnetic stirrer and dropping funnel 13.45 g (94.60 mmol) *tert*-butyl methacrylate and 0.75 g (4.54 mmol) AIBN were dissolved in 2-butanone to give a 32 wt.% solution. The flask was thermostated at 80 °C and a solution of 4.675 g (41.71 mmol) itaconic acid anhydride (32 wt.%) and 1.49 g (9.09 mmol) AIBN in 2-butanone was added dropwise within 6 h. The polymerisation was continued for another 48 h, the polymer precipitated from the tenfold amount of cyclohexane and dried in vacuo (50 °C, 0.05 mbar) for 12 h. The yield was 7.635 g (42% of the theoretical yield), the polymer had 85 mol% *tert*-butyl methacrylate and 15 mol% itaconic acid anhydride.

IR: 2978, 2934 (ν(C–H)); 1861, 1782 (ν(C=O) anhydride); 1719 (ν(C=O) ester); 1143 (ν(C–O)); 980 cm^{-1}.
^{1}H-NMR: ($CDCl_3$): δ=0.60–1.33 (3H, CH_3), 1.33–1.67 (9H, $C(CH_3)_3$), 1.67–2.54 (2H, $–CH_2–$), 2.60–3.20 ppm (2H, $–CH_2–$).
^{13}C-NMR: ($CDCl_3$): $\delta = 17.6$, 18.3 ($–CH_3$), 27.65 ($–C(\mathbf{C}H_3)_3$), 46.1 (s, $–C–\mathbf{C}H_2–CO$) 49.0–56.0 ($–CH_2–$), 80.7 ($–\mathbf{C}(CH_3)_3$), 82.4 ($–CO–\mathbf{C}–CH_2$), 169.1 (—C=O (anhydride)), 177.1 ppm (—C=O (ester)).

2.2. Alcoholysis (general procedure)

In a flame dried nitrogen flask the polymer was dissolved in toluene, 2-butanone or 2-methoxy methyl ethyl acetate (MPA), the calculated amount of alcohol and catalyst was added, the flask closed and stirred at given temperatures for given times (Table 3). The polymers were precipitated from the tenfold amount of cyclohexane and dried in vacuo at 50 °C/0.05 mbar to constant weight.

Poly(*tert*-butyl methacrylate-co-mono methyl itaconate).

IR: 2977, 2953, 2880 (ν(C–H) overlapping with very broad OH-absorption); 1723 (ν(C=O)); 1143 cm^{-1} (ν(C–O)).
^{1}H-NMR: (DMSO-d_6): $\delta = 0.5$–1.3 (–CH_3, 3H); 1.38 (–$C(CH_3)_3$, 9H); 1.4–3.0 (–CH_2-backbone, 2H); 3.50 ppm (–CH_2-itaconic acid, 2H).
^{13}C-NMR: (DMSO-d_6): $\delta = 17.8$ (–C–**C**H_3); 27.6 (–C(**C**H_3)$_3$); 45.9 (–**C**H_2–CO); 51.1 (O–CH_3); 30.0–58.3 (–CH_2–); 80.8 (–**C**$(CH_3)_3$); 175.5 (C=O, ester), 177.5 ppm (C=O, anhydride).

Poly(*tert*-butyl methacrylate-co-mono 2-propenyl itaconate).

IR: 2978, 2936 (ν(C–H) overlapping with very broad OH-absorption); 1858, 1783 (ν(C=O) anhydride); 1721 (ν(C=O) ester); 1144 cm^{-1} (ν(C–O)).
^{1}H-NMR: (DMSO-d_6): $\delta = 0.99$ (–CH_3 isopropyl ester, 3H); 1.20 (–CH_3 *tert*-butyl ester 3H); 1.41 (–$C(CH_3)_3$, 9H); 1.4–3.0 (–CH_2-backbone, 2H); 2.79 (–CH_2-itaconic acid, 2H); 4.94 ppm (–CH, 1H).
^{13}C-NMR: (DMSO-d_6): $\delta = 18.2$ (–C–**C**H_3); 21.7 (–CH(**C**H_3)$_2$); 27.7 (–C(**C**H_3)$_3$); 46.1 (–C–**C**H_2–CO anhydride); 47.3 (–C–CH_2–CO– ester); 50.0–56.0. (–CH_2–); 80.8–82.4 (–**C**$(CH_3)_3$); 169.2 (C=O, anhydride); 176.3 ppm (C=O, ester and acid).

2.3. Thermal re-formation of anhydride in polymer film

Films of the polymers obtained from alcoholysis were prepared on sodium chloride plates for IR-spectroscopy. They were kept at 120 °C (methyl ester) and 100 °C (isopropyl ester), respectively, on a hot-stage in the spectrometer. During a period of 20 in case of the methyl ester and 75 min for the isopropyl ester spectra were measured with a delay of 20 s in between. The spectra were normalized to the absorption of residual *N*,*N*-dimethylaminopyridine at 1649 cm^{-1} and the increase of the height of the absorption at 1861 cm^{-1} (ν_{sym}(C=O) anhydride) was followed.

IR: 2978, 2934, 2880 (ν(C–H) overlapping with very broad OH-absorption); 1861, 1782 (ν(C=O) anhydride); 1719 (ν(C=O) ester); 1649 ((ν(C=CH) residual *N*,*N*-dimethylaminopyridine); 1143 cm^{-1} (ν(C–O)).

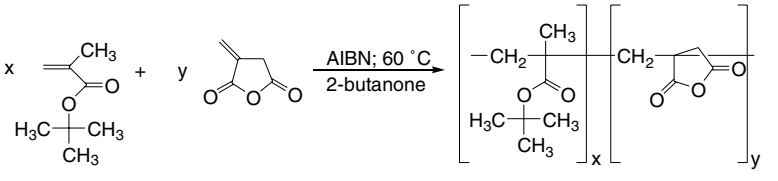
3. Results and discussion

3.1. Copolymerisation of tert-butyl methacrylate with itaconic anhydride and reactivity ratios

Itaconic acid anhydride and *tert*-butyl methacrylate were copolymerised in 2-butanone at 60 °C using 0.01 mol% of AIBN as initiator with respect to the total amount of monomers (cf. Scheme 1). Comonomer ratios were calculated from the method described by Kelen and Tüdős [22]. As reactivity ratios r_1 0.138 and r_2 3.88 were used, which were calculated from the tabled *Q*, *e* values [23]. Some of the polymerisations had conversion above 15%, they were repeated with practically identical monomer composition. All polymers could be isolated by precipitation from cyclohexane. Monomer ratios, reaction conditions, yields and analytical data of the copolymers are included in Table 1.

The infrared-spectra of the copolymers show carbonyl absorptions of the anhydride group at 1861 (ν_{sym}) and 1782 cm^{-1} (ν_{asym}), of the ester at 1719 cm^{-1} and the C–O-absorption at 1143 cm^{-1}. The absence of an COOH/OH-absorption between 3500 and 2200 cm^{-1} proves that the copolymers are free of acid which can be seen from Fig. 1. Copolymer compositions were calculated from ^{1}H-NMR-spectra of which an example is given in Fig. 2. The ratio of signal of the CH_2-group in the anhydride ring (between 3.20 and 2.60 ppm) to the sum of all other protons was used. The signal of the *tert*-butyl ester protons alone (between 1.60 and 1.20 ppm) cannot be used for integration as it is overlapping with the protons of the CH_2-group of the polymer chain (2.50–1.60 ppm) at lower field and the methyl protons of the ester at higher field (0.6–1.2 ppm). The data were cross-checked by comparison to data obtained from inverse-gated ^{13}C-NMR-spectra.

The reactivity ratios were calculated using the method reported by Kelen and Tüdős. (Table 2) [24]. This method has the advantage that it can be used also, if conversion is higher than 10% [25]. Entries **4** and **6**–**9** of Table 1 have been used for the calculation. The reactivity ratio r_1 for itaconic anhydride is 0.272 that of *tert*-butyl methacrylate r_2 is 0.300. The experimental values are completely different from those obtained from the *Q*, *e* values (Table 3). This might be due to polar



Scheme 1. Copolymerisation of itaconic anhydride **1** and *tert*-butyl methacrylate **2**.

Table 1
Copolymers from *tert*-butyl methacrylate **1** and itaconic anhydride **2**

No.	Monomer in feed		f_1	Yield (%)	t (min)	F_1	DSC-peak (°C)	Mass loss/% (temperature range (°C))	T_g (°C)	Enthalpy (DSC) (J g^{-1})	M_n (M_w) (10^4 g mol^{-1}) (*D*)
	1/g (mmol)	**2**/g (mmol)									
3	5.149 (45.9)	4.185 (29.4)	0.609	23.78	60	0.412	173	18.8 (158–181)	128	144	0.58 (1.16) *2.00*
4	4.584 (40.9)	2.661 (18.7)	0.686	14.71	60	0.439	171	17.3 (156–182)	129	150	–
5	1.753 (15.6)	4.132 (29.1)	0.349	3.70	45	0.532	186	33.3 (177–212)	137	203	–
6	1.343 (12.0)	3.228 (22.7)	0.346	14.66	60	0.552	188	28.4 (175–250)	127	244	1.40 (2.91) *2.07*
7	1.880 (16.8)	4.519 (31.8)	0.346	3.15	30	0.618	199	32.3 (186–226)	116	272	2.82 (6.76) *2.40*
8	0.502 (4.5)	4.547 (32.0)	0.123	13.16	60	0.748	214	32.9 (200–254)	119	338	3.12 (5.93) *1.90*
9	0.063 (0.6)	4.870 (34.2)	0.016	5.90	60	0.868	227	42.2 (216–244)	121	343	5.41 (8.71) *1.61*
10	0.234 (2.9)	4.455 (31.3)	0.085	19.67	60	0.962	242	42.2 (231–258)	116	458	–
11	13.45 (94.6)	4.68 (41.7)	0.694	42.11	3240	0.850	216	–	119	282	8.64 (17.98) *2.08*

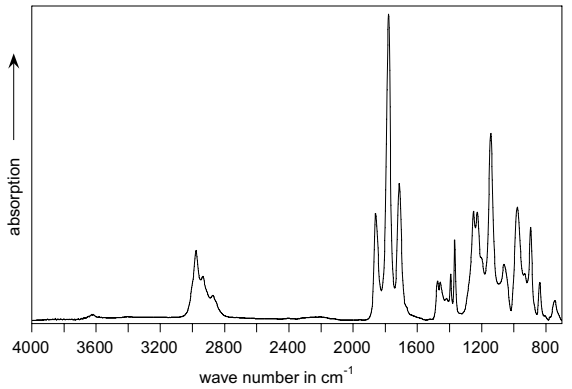


Fig. 1. IR-spectrum of poly(*tert*-butyl methacrylate-stat-itaconic acid anhydride).

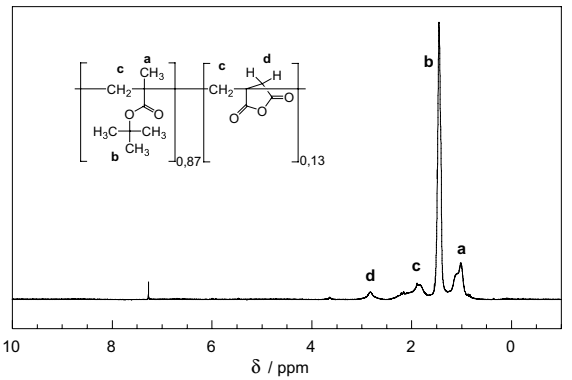


Fig. 2. H-NMR-spectrum of poly(*tert*-butyl methacrylate-stat-itaconic acid anhydride).

Table 2
Reactivity ratios

r_1	r_2	Statistics	
0.272	0.301	$\Delta r_1 = 0.08$	$\Delta r_2 = 0.09$
		$\delta = 0.080$	$Q_{KT} = 16.089$

interactions between the two monomers or between the monomers and the solvent.

The copolymer composition diagram in Fig. 3 shows that the copolymerisation is statistical with an azeotropic point at a feed ratio of *tert*-butyl methacrylate/itaconic anhydride of 0.96, which is almost equimolar.

In contrast the copolymerisation of maleic anhydride and *tert*-butyl methacrylate shows non-azeotropic copolymerisation behaviour with preferential incorporation of the ester **1**, as maleic anhydride cannot be homopolymerised [26]. This limits its content in copolymers to 50% which would be an alternating copolymer. Itaconic anhydride *tert*-butyl methacrylate copolymers have longer anhydride sequences, while maleic anhydride is always incorporated in a sequence length of one. Longer anhydride sequences should ease the reaction with amino functional siloxanes as the anhydride groups are not surrounded by bulky *tert*-butyl groups as is the case for maleic anhydride. Furthermore neighbouring anhydride groups create a more polar environment of the reacting anhydride which should also simplify the reaction with polar reactants.

3.2. Properties of the copolymers

Molar masses of the copolymers relative to polystyrene standards are in the range from 0.58×10^4 to

Table 3
Alcoholysis of poly(*tert*-butyl methacrylate-stat-itaconic acid anhydride)

No.	Alcohol	Anhydride/OH (% alcoholysis expected)	T (°C)	Solvent	Polymer	Catalyst	t/h	Result
12	Isopropanol	1:1 (100)	20	2-Butanone	**11**	−	48	No alcoholysis
13		1:0.13 (8)	20	2-Butanone	**11**	−	48	No alcoholysis
14		1:28 (100)	70	Toluene	**11**	+	16	Very few
15		1:28 (100)	70	Toluene	**11**	−	16	No alcoholysis
16	Methanol	1:43 (100)	60	Toluene	**3**	+	112	Complete
17		1:44 (100)	60	Toluene	**3**	−	112	Complete
18	Isopropanol	1:1.1 (100)	60	Toluene	**11**	+	122	Partial
19		1:0.9 (43)	60	Toluene	**11**	+	162	Partial

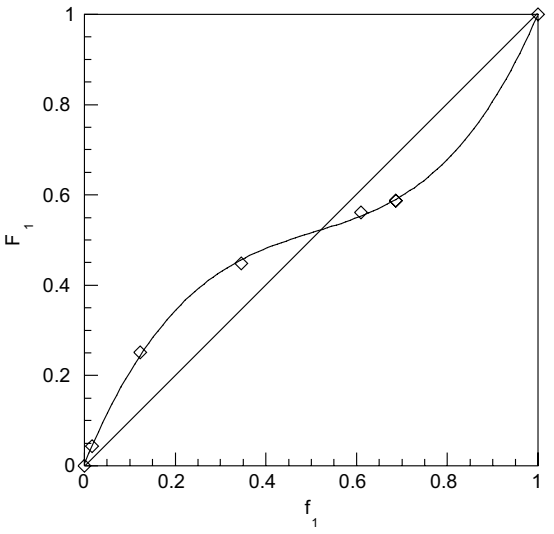


Fig. 3. Copolymer composition diagram of poly(*tert*-butyl methacrylate-stat-itaconic acid anhydride); data points (◇), calculated (curve).

5.41×10^4 g/mol. They increase with increasing anhydride content of the polymer. This may be due to chain transfer activity of the *tert*-butyl ester. M_w/M_n ratios are in the order of two with the exceptions of one higher and one lower value 1.61 and 2.40 without any relation to copolymer composition.

Glass transition temperatures obtained from differential scanning calorimetry (DSC) are between 116 and 137 °C. Again no relationship to copolymer composition can be found. The values scatter around the temperature range of the glass transition temperatures of the homopolymers, 129 °C for poly(itaconic anhydride), 114 °C for poly(*tert*-butyl methacrylate).

The DSC traces of the copolymers (cf. Fig. 4) further have an endotherm between 171 and 242 °C which is caused by ester cleavage (thermal *cis*-elimination of isobutylene). Peak temperature and enthalpy increase proportional to the *tert*-butyl methacrylate content as

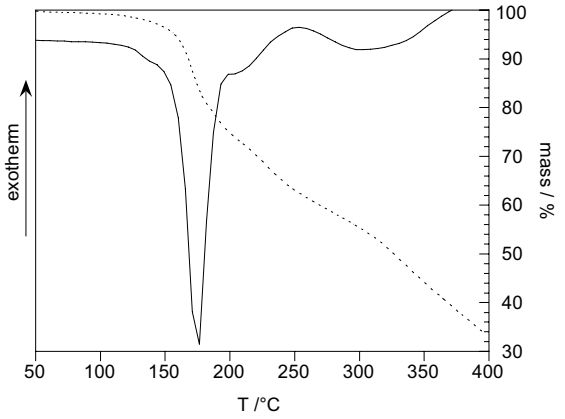


Fig. 4. DSC- and TGA-diagram of copolymer **4** (Table 1) containing 56.1 mol% anhydride.

shown in Fig. 5. The relation for the enthalpy is as expected, the increase of the peak temperature of the reaction endotherm is most likely caused by a small amount of acid groups formed by the anhydride during handling which catalyses the ester cleavage. The

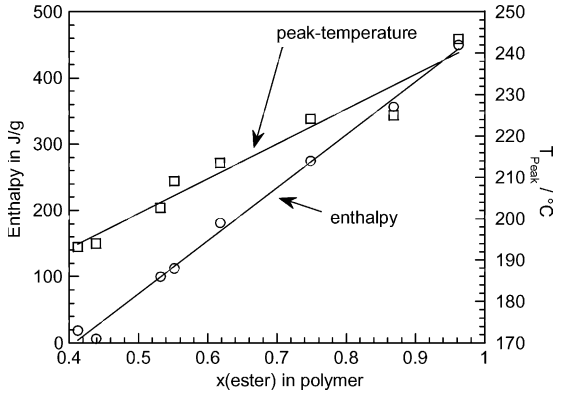


Fig. 5. Enthalpy and peak temperature (DSC) vs. ester content of copolymer.

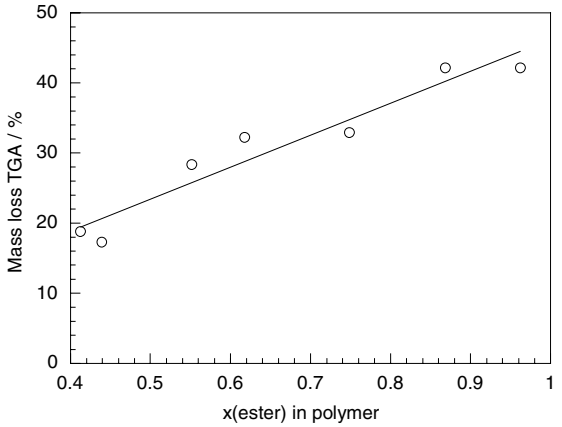


Fig. 6. Mass loss (TGA) vs. ester content of copolymer.

endothermic signal in the DSC is connected to a mass loss in thermogravimetry (TGA) in the same temperature range. The mass loss can be correlated to the copolymer composition giving an easy estimate of the ester content of the copolymer (Fig. 6). Due to the subsequent anhydride formation by adjacent acid groups, which gives water as side-product, this method is not very accurate. The conversion of acid groups depends on statistics and the sequence distribution of the comonomers along the polymeric chain.

3.3. Alcoholysis of the copolymers

Anhydrides react with alcohols to give an ester and an acid moiety, in case of cyclic anhydrides monoester acids are formed (Scheme 2). There are several papers dealing with the copolymerisation of monoalkyl itaconates and the thermal properties of the copolymers [27,28]. An alternate way to obtain such copolymers would be polymer analogous alcoholysis of itaconic anhydride containing polymers (Scheme 2).

Two copolymers of *tert*-butyl methacrylate and itaconic anhydride were used for the polymer analogous alcoholysis obtained by free radical copolymerisation to higher conversion. One had an ester content of 85% and was synthesized by a copolymerisation procedure with stepwise addition of the anhydride (polymer **11** in Table 1), the second one of 41% (polymer **3** in Table 1). Both polymers were used for alcoholysis with isopropanol and methanol.

First experiments were done by simply adding isopropanol to the solution obtained at the end of polymerisation after cooling to 20 °C (Table 3). No alcoholysis was found proving that the copolymers could be precipitated from isopropanol. In toluene as solvent no alcoholysis with isopropanol could be found at 70 °C without catalyst. With 4-dimethylamino pyridine (DMAP) as catalyst only minor reaction was found after 16 h at 70 °C. Conversion could be increased by longer reaction times but even after six days alcoholysis was far from complete. In contrast methanol gives complete alcoholysis even in the absence of catalyst after 112 h at 60 °C (Table 3). In Fig. 7 the IR-spectrum of the polymer from experiment **16** before and after alcoholysis is shown. The absorptions of the anhydride group in the carbonyl region have completely disappeared and a broad OH-absorption between 3800 and 2400 cm^{-1} proves the formation of an monoalkyl itaconate. The *tert*-butyl ester carbonyl band at 1719 cm^{-1} is broadened as it is convoluted with the C=O-absorption of the methyl ester formed.

3.4. Thermal properties of the monoalkyl itaconate copolymers

The DSC-traces of copolymer **3** before and after alcoholysis (experiment **16**) are shown in Fig. 8. Before alcoholysis the copolymer has an endothermic signal

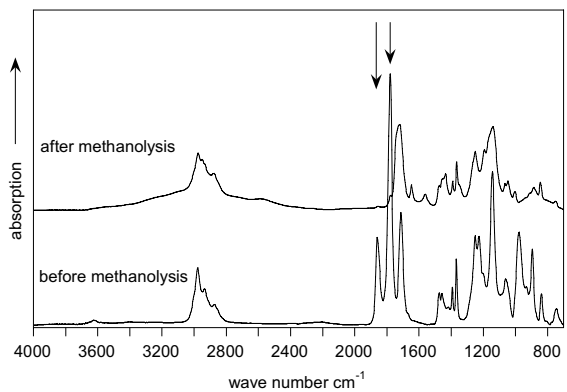
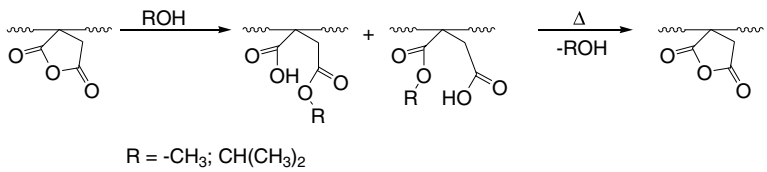


Fig. 7. IR-spectrum of **16** before and after methanolysis.



Scheme 2. Polymeranalogous alcoholysis and reformation of anhydride from poly(*tert*-butyl methacrylate-stat-itaconic acid anhydride).

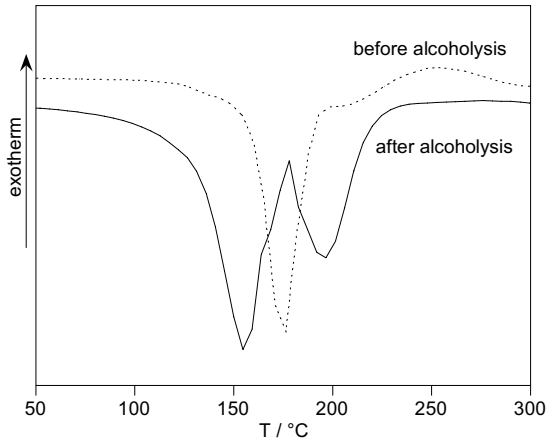


Fig. 8. DSC-plots of **16** before and after alcoholysis.

with a peak temperature of 173 °C. After methanolysis two endotherms are visible with peak temperatures of 154 and 196 °C, respectively. Corresponding to this there are now two steps in the TGA curve giving a higher mass loss than in starting polymer (Fig. 9). The lower temperature mass loss is smaller than the second; it is caused by the reverse reaction of the monoester acid to the cyclic anhydride. The anhydride is formed back (Scheme 2) and methanol evaporates causing the mass loss in TGA. The latter is caused by the cleavage of the *tert*-butyl ester and almost equal to that of the original polymer. Hence the cleavage temperature of the *tert*-butyl ester is shifted towards higher temperatures. This cannot be explained at present as one would expect a decrease rather than an increase because of the high amount of acid groups present in the monoalkyl itaconate containing polymer.

The easy formation of anhydride moieties from the monoalkyl itaconate groups (Scheme 2) offers interesting

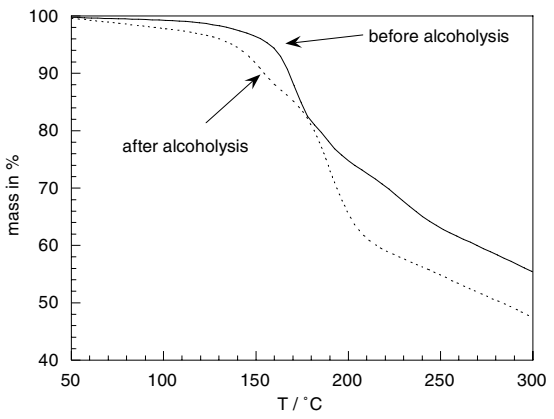


Fig. 9. TGA-plots of **16** before and after alcoholysis.

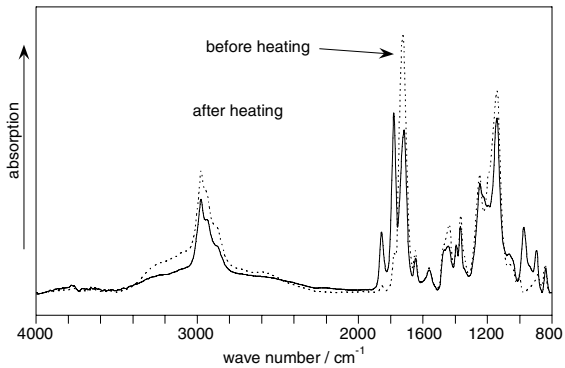


Fig. 10. IR-spectrum of **16** after alcoholysis and after recyclisation.

possibilities for applications in microlithography with polymer films. To study this, films of alkyl itaconate containing polymers were prepared on silicon discs for IR-spectroscopy. The films were heated on a hotstage in the spectrometer and spectra were taken in a multiscan mode. Fig. 10 shows the IR-spectra of the polymer from experiment **16** before and after heating to 120 °C. The spectra clearly indicate that anhydride is formed. The absorptions of anhydride groups at 1861 and 1782 cm^{-1} are formed while the COOH-absorption between 2800 and 2400 cm^{-1} decrease in intensity. There is no ester cleavage of the *tert*-butyl ester observed proving that the cleavage of the *tert*-butyl ester is really shifted to elevated temperature. Formation of anhydride was not quantitative; an estimate of conversion was made assuming that the anhydride absorption and the ester absorptions have a linear correlation to the content of these groups in copolymer. The estimation is rather difficult as the absorption of the ester and acid carbonyl groups formed by alcoholysis can not be separated from the ester band of the *tert*-butyl ester. But using integration of the anhydride band at 1861 cm^{-1} vs. the sum of the ester and acid bonds before alcoholysis, after alcoholysis, and after anhydride re-formation indicate that the conversion is roughly 80–85%. A time conversion diagram of anhydride formation is shown in Fig. 11 using the height of the anhydride band at 1861 cm^{-1} as a measure of concentration. Attempts to derive a kinetic equation proved complex behaviour and no simple zero, first- or second-order kinetics. This can be understood if one takes into account that the reaction takes place below the glass transition temperature in the solid polymer. A possible equation to describe the curve is

$$\text{height} = 0.48(1 - e^{-0.13t})$$

Similar results were found investigating the re-formation of anhydride in monoisopropyl itaconate copolymers

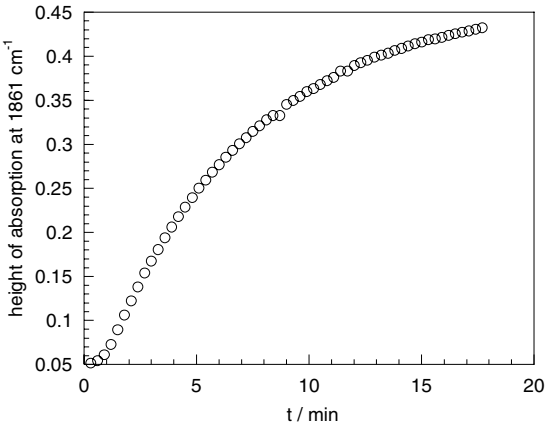


Fig. 11. Re-formation of anhydride at 120 °C; polymer from methanolysis.

but the reaction is slower than that of monomethyl itaconates.

The experiments show that the formation of anhydride from monoalkyl itaconates is possible. It is remarkable that this re-formation of anhydride proceeds with reasonable rate already at temperatures far below the lowest temperature found for cleavage of the *tert*-butyl ester in these copolymers. This opens the possibility to adjust resist properties like solubility and adhesion during the lithographic process. Adhesion could be improved introducing polar groups by alcoholysis. A baking step during processing could be used to form anhydride groups from a certain percentage of monoalkyl itaconate. This would give a more hydrophobic polymer, reactive groups in the CARL process and probably lower glass transition temperature.

4. Conclusions

Copolymers from itaconic anhydride (**1**) and *tert*-butyl methacrylate (**2**) have been synthesized by free radical copolymerisation. The reactivity ratios were 0.272 ± 0.08 for the ester and 0.301 ± 0.09 for the anhydride showing that it is an azeotropic copolymerisation with an azeotropic point at almost equimolar feed ratio. DSC showed linear correlations between peak temperature and enthalpy of the endotherm for the cleavage of the *tert*-butyl ester and its content in the copolymer. Alcoholysis of anhydride with isopropanol and methanol gave monoalkyl itaconates with complete conversion for methanol and low conversion for isopropanol. *N*,*N*-dimethyl-aminopyridine catalyses the alcoholysis and is necessary in case of isopropanol. Re-formation of the anhydride is possible at 100 °C in case of the monoisopropyl ester and 120 °C for the monomethyl ester. Anhydride formation in films did not go to 100% conversion, it is faster in case of monomethyl ester, the monoisopropyl ester reacts slower and gives only little conversion. These reactions offer the option to reversibly adjust polymer properties, e.g. glass transition temperature and solubility. In particular in photoresist process the adhesion and solubility properties can be optimised during manufacture by simple alcoholysis and baking steps.

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