ELSEVIER

Polymer 44 (2003) 527–533

polymer

www.elsevier.com/locate/polymer

# Copolymers from *tert*-butyl methacrylate and 2-propenyl isocyanate—polymers for photoresist application

Jens Ferbitz, Werner Mormann*

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

Received 19 June 2002; received in revised form 18 October 2002; accepted 24 October 2002

**Abstract**

Free radical copolymerisation of *tert*-butyl methacrylate (**1**) with 2-isopropenyl isocyanate (**2**) has been investigated. Reactivity ratios of $r_1 = 3.48 \pm 0.60$ for **1** and $r_2 = 0.004 \pm 0.04$ for **2** were obtained. As 2-propenyl isocyanate has almost no tendency to homopolymerise maximum isocyanate content is reached in an alternating copolymer. The reaction of the isocyanate functionality with morpholine was used to obtain compounds for determination of the composition by NMR-spectroscopy. Glass transition temperature of the copolymers increases with increasing *tert*-butyl methacrylate content. It was found that thermal *cis*-elimination of isobutylene from the *tert*-butyl ester is followed by two further reactions: formation of six-membered anhydride rings by two neighbouring acid functionalities and formation of 3,4-dimethyl-pyrrolidin-2-one from one acid group and an adjacent isocyanate functionality. The reactions could be observed in the solid state and in solution at about 200 °C. Molecular weights of the copolymers as determined by size exclusion chromatography decreases with increasing isocyanate content which is due to chain transfer reactions of isopropenyl isocyanate. Conversion per minute decreases with increasing isocyanate content in the monomer feed.


*Keywords:* Copolymerisation; Anhydride formation; Photoresist

## 1. Introduction

*tert*-Butyl methacrylate is one of the standard monomers with an acid labile group in positive photoresists for 193 nm microlithography. Homopolymerisation of the *tert*-butyl ester has been reported [1], block copolymers and random copolymers with *tert*-butyl methacrylate are also known [2,3].

In microlithography based on a bilayer process, e.g. the CARL process which was introduced by Sebald et al. in 1990 (CARL: *C*hemical *A*mplification of *R*esist *L*ines), film patterning is made with a separate liquid phase silylation step after development of the resist [4]. In this step α,ω-bisaminopropyl-oligodimethyl-siloxane reacts with suitable reactive functional groups in the base resin to form a cross-linked network. In a following oxygen plasma etch step the silicon enriched resist is converted into etch resistant silicon oxide. Moreover, the silylation step causes shrinkage of hole structures and widening of line patterns ('chemical biasing') which extends the resolution limits. In the CARL process anhydrides are mainly used as reactive sites for the silylation.

A possible alternative is the isocyanate functionality as isocyanates are known to react very fast with amines [5]. During our studies on photoresists for 193 and 157 nm microlithography we proved that isocyanates are suitable reactive sites for wet-silylation and that they are more reactive than anhydrides towards α,ω-bisaminopropyl-oligodimethyl-siloxanes [6]. Isocyanates suitable for free radical polymerisation are for example vinyl isocyanate and 2-propenyl isocyanate. As vinyl isocyanate has a low boiling point (45 °C) and higher toxicity 2-propenyl isocyanate (bp 64 °C) is the better choice. 2-Propenyl isocyanate has first been synthesised by Hart [7]. It does not homopolymerise; copolymers with maleic anhydride and trimethylsilyl methacrylate have already been described in previous papers from our laboratory [8,9]. Copolymers with *tert*-butyl methacrylate have not been reported in the literature to date. For a controlled synthesis of resist polymers with 2-propenyl isocyanate knowledge of the copolymerisation behaviour of this monomer with possible comonomers is a prerequisite.

* Corresponding author. Tel.: +49-271-740-4713; fax: +49-271-740-2226.

*E-mail address:* mormann@chemie.uni-siegen.de (W. Mormann).

0032-3861/03/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00799-1

The present paper describes the copolymerisation of 2-propenyl isocyanate with *tert*-butyl methacrylate, properties of the copolymers and reactions that occur on heating or in the presence of an amine.

## 2. Experimental part

### 2.1. Methods of characterisation

IR-spectra were recorded on a Bruker Equinox 55 FTIR spectrometer, $^{1}H/^{13}C$ NMR-spectra (Bruker AC-400) were obtained in deuterochloroform with $CHCl_3$ or tetramethylsilane as internal standard. Thermal properties were determined on a Mettler TA 4000 System with DSC 30 and TG 50 equipment. Size exclusion chromatography (SEC) was performed with a PSS-System 2000, with a UV-detector Lambda 1010 and 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.

### 2.2. Materials

*tert*-Butyl methacrylate (TCI, Japan) was purified by distillation over calcium hydride in vacuo before use. Methacryloyl chloride was obtained from ACROS and freshly distilled prior to use. AIBN was recrystallised in diethyl ether before use. Benzene was purified by distillation over calcium hydride and toluene was distilled over sodium. Other solvents used were dried according to literature procedures. All reactions were made in flame dried glass equipment in an atmosphere of dry argon.

2-*Propenyl isocyanate* (**2**) was synthesised from methacryloyl chloride and sodium azide as reported by Hart [7]. It was freshly distilled in vacuo before use.

Yield: 87%; Lit.: 69%
bp: 64 °C/1013 mbar
IR: 2267 ($\nu_{as}$(NCO)), 1650 $cm^{-1}$ ($\nu$(C=C)
$^{1}H$ NMR: ($CDCl_3$): $\delta = 1.98$ (s, 3H, $CH_3$), 4.58 and 4.71 ppm (s, 2H, $=CH_2$)
$^{13}C$ NMR: ($CDCl_3$): $\delta = 23.38$ (s, $CH_3$), 106.41 (s, $=CH_2$), 124.15 (s, NCO), 134.62 ppm (s, $CH_2=C$))

### 2.3. Copolymerisation of tert-butyl methacrylate and 2-propenyl isocyanate

In a 25 ml flame dried nitrogen flask *tert*-butyl methacrylate and 2-propenyl isocyanate were dissolved in dry toluene to give a concentration of 20 mmol monomer in 1 ml solvent. AIBN was added in a molar ratio of 1:100 referring to the total amount of monomer and the mixture degassed in three freeze-pump-thaw cycles. Polymerisation was performed at 60 °C for 20 min. The polymer was isolated by repeated freeze-drying from 200 ml dry benzene. Details of the experiments are given in Table 1.

IR: 2977, 2935 ($\nu$(C–H)), 2262 ($\nu_{as}$(NCO)), 1721 ($\nu$(C=O)), 1140 $cm^{-1}$
$^{1}H$ NMR: ($CDCl_3$): $\delta = 0.4–1.3$ (3H, $CH_3$), 1.3–1.6 (9H, $-C(CH_3)_3$), 1.6–1.9 (2H, $-CH_2-$ (ester)), 1.9–2.3 ppm (2H, $-CH_2-$ (isocyanate))
$^{13}C$ NMR: ($CDCl_3$): $\delta = 16.72$ and 17.41 (m, $CH_3$ (ester)), 22.41 (s, $CH_3$ (isocyanate)), 26.77 (s, $-C(CH_3)_3$), 45.19 (s, $C$–NCO), 49.0–56.0 (m, $-CH_2-$), 58.46 (s, NCO), 79.81 (s, $-C(CH_3)_3$), 175.68 and 176.20 (m, C=O)

### 2.4. Polymeranalogous reactions

#### 2.4.1. Synthesis of poly(tert-butyl methacrylate-co-morpholine-4-carboxylic acid 2-propenyl-amide) 3a–8a

In a 25 ml flame dried nitrogen flask 0.1–0.25 g of poly(*tert*-butyl methacrylate-*co*-2-propenyl isocyanate) (**3**–**8**, Table 1) were dissolved in toluene to give a 10% (weight by weight) solution. Morpholine in slight excess with respect to the highest possible content of isocyanate in copolymer was added. The mixture was stirred for 19 h at room temperature and complete conversion of isocyanate was checked by IR-spectroscopy. The polymers were isolated by precipitation in the tenfold amount of pentane and subsequent freeze-drying from 100 ml benzene.

IR: 3540 ($\nu$(NH)), 2933, 2854 ($\nu$(CH)); 1721 ($\nu$(C=O)); 1140 $cm^{-1}$ ($\nu$(C–O))
$^{1}H$ NMR: ($CDCl_3$): $\delta = 0.5–1.3$ (3H, $CH_3$), 1.3–1.6 (9H, $C(CH_3)_3$), 1.6–2.5 (2H, $-CH_2-$ (backbone)), 3.0–4.0 ppm (2H, $CH_2$ (morpholine))
$^{13}C$ NMR: ($CDCl_3$): $\delta = 17.7$ and 19.6 (m, $CH_3$ (ester)), 23.4 (s, $CH_3$ (isocyanate)); 27.7 (s, $C(CH_3)_3$), 43.8 (s, C–NH), 46.1 (s, $-CH_2-N-CH_2$), 49.0–58.0 (m, $-CH_2-$), 66.6 (s, $-CH_2-O-CH_2-$), 80.7 (s, $C-C(CH_3)_3$), 156.0 (s, $-NH-(C=O)-NH-$), 177.2 ppm (m, C=O)

#### 2.4.2. Cyclisation reaction of poly(tert-butyl methacrylate-co-2-propenyl isocyanate)

*Reaction in solution*: 0.594 g of poly(*tert*-butyl methacrylate-*co*-2-propenyl isocyanate) were dissolved in 19.6 g diphenyl-ether and heated to 200 °C for 6 h. A white solid precipitated during the reaction. The mixture was poured into 200 ml of dry benzene and stirred for 60 h at room temperature. The mixture was filtered in an argon atmosphere and the solid was dried in vacuo at 0.05 mbar for 16 h.

IR: 3448 ($\nu$(NH) overlapping with a broad COOH-absorption), 2987 ($\nu$(CH) overlapping with a broad COOH-absorption), 1803, 1759 ($\nu$(C=O) anhydride), 1718 ($\nu$(C=O) pyrrolidine-2-one), 1157 ($\nu$(C–O)); 1021 $cm^{-1}$
$^{1}H$ NMR: (DMSO-$d_6$): $\delta = 1.19$ ppm (3H, $-CH_3$), 1.84

Table 1
Copolymerisation of *tert*-butyl methacrylate (**1**) and 2-propenyl isocyanate (**2**)

| No. | $f_2$ | $F_2$ | Yield (%) | DSC-peak (°C) | | DSC-enthalpy (J/g) | | $T_g$ (°C) | TGA-mass loss (%) | $M_n$ ($M_w$) ($10^3$ g/mol), $D$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Exo | Endo | Exo | Endo | | | |
| **3** | 0.916 | 0.439 | 6.07 | 234 | 252 | 92 | 0 | 56 | 33.66 | 1.64 (2.78), 1.70 |
| **4** | 0.750 | 0.339 | 7.80 | 238 | 253 | 22 | 75 | 79 | 40.13 | 2.26 (5.42), 2.40 |
| **5** | 0.701 | 0.290 | 7.50 | 238 | 252 | 9.6 | 102 | 85 | 41.92 | 2.52 (5.37), 2.13 |
| **6** | 0.514 | 0.212 | 13.90 | – | 251 | – | 160 | 86 | 43.84 | 2.88 (6.52), 2.27 |
| **7** | 0.289 | 0.170 | 12.63 | – | 252 | – | 360 | 100 | 42.86 | 3.55 (7.38), 2.08 |
| **8** | 0.399 | 0.079 | 21.49 | – | 252 | – | 451 | 114 | 43.58 | 4.90 (11.44), 2.33 |

(2H, $-CH_2-$); 3.31 (1H, NH); 12.72 ppm (1H, COOH) $^{13}$C NMR: (DMSO-$d_6$): $\delta = 16.6$ (s, $-CH_3$ (acid)), 18.6 (m, CO–C–$CH_3$ (pyrrolidine-2-one)), 20.1–29.0 (m, $-CH_3$ (anhydride)), 30.7 (m, NH–C–$CH_3$), 42.9 (s, $-CH_2-$ (anhydride)); 44.2 (m, $-CH_2-$ (pyrrolidine-2-one)), 49.0 (m, $-CH_2-$), 172.0 (m, C=O (anhydride)), 177.8 ppm (m, NH–C=O)

*Reaction in film*. A film of poly(*tert*-butyl methacrylate-*co*-2-propenyl isocyanate) (polymer **3** from Table 1) was prepared on a sodium chloride plate and heated to 210 °C on a hotstage in the IR-spectrometer for 2 h. IR-spectra were taken before and after heating.

IR: 3448 ($\nu$(NH) overlapping with a broad COOH-absorption), 2987 ($\nu$(CH) overlapping with a broad COOH-absorption), 1803, 1759 ($\nu$(C=O) anhydride), 1718 ($\nu$(C=O) pyrrolidine-2-one), 1157 ($\nu$(C–O)); 1021 $cm^{-1}$

## 3. Results and discussion

### 3.1. Synthesis of copolymers and reactivity ratios

In order to optimise data points for calculation of the reactivity ratios monomer feeds were calculated according to the method described by Kelen–Tüdös [10]. Free radical copolymerisation of isopropenyl isocyanate with *tert*-butyl methacrylate was made in a solution of the monomers in toluene and with 1 mol% of α,α′-azodiisobutyronitrile (AIBN) as initiator at 60 °C for 20 min. The polymers were isolated by repeated freeze-drying from benzene. The experimental data are summarized in Table 1.

The yields were between 6 and 21%; they increased with increasing *tert*-butyl methacrylate content in feed. This indicates that the ester reacts faster than the isocyanate, which is also supported by the lack of homopolymerisation of this monomer. The correlation of rate of polymerisation (conversion per minute) versus *tert*-butyl ester content in feed is given in Fig. 1. Up to 30% *tert*-butyl methacrylate in feed the rate of polymerisation is almost constant. At higher ester content a huge increase in conversion per minute is observed.

The IR-spectra of the copolymers show the absorption of the isocyanate group at 2262 $cm^{-1}$ and of the carbonyl group at 1721 $cm^{-1}$. In the proton nuclear magnetic resonance spectrum the signal of the methyl group is at 0.4–1.6 ppm, that of the *tert*-butyl group at 1.3–1.6 ppm, those of the methylene groups of the ester from 1.6 to 1.9 ppm and for the isocyanate from 1.9 to 2.3 ppm. The last two signals cannot be separated for integration.

In the carbon NMR-spectra of the copolymers the signals of the methyl groups appear at 16.7 and 17.4 ppm for the ester and 22.4 ppm for the isocyanate. The signal of the *tert*-butyl group is found at 26.8 ppm and that of the quaternary carbon next to the NCO-group at 45.2 ppm. The methylene groups show a number of signals between 49 and 56 ppm, the signal of the isocyanate carbon is found at 58.5 ppm. The resonances of the quaternary carbon of the *tert*-butyl group (79.8 ppm) and of the carbonyl carbon (175.7 and 176.2 ppm) are at lower field. As the NMR-spectra of the copolymers are not suited for calculation of the copolymer composition, the isocyanate groups were transformed to urea moieties in a polymeranalogous reaction with morpholine (Scheme 1).

The reactions were performed at room temperature with

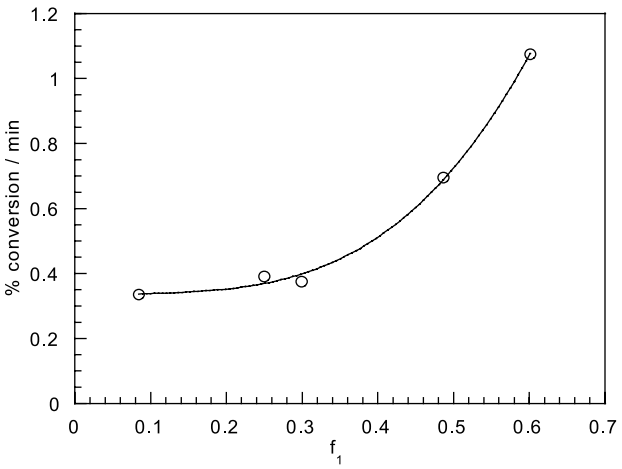
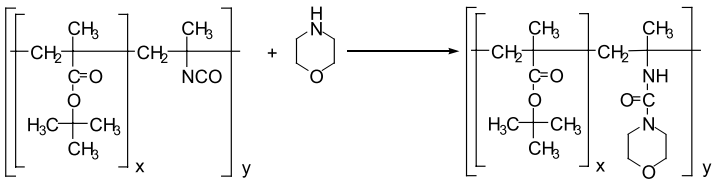



Fig. 1. Rate of polymerisation (conversion per minute) as function of *tert*-butyl methacrylate in the feed.



Scheme 1.

a slight excess of morpholine. After 19 h in all cases full conversion of the isocyanate group was reached, which was proven by complete absence of the isocyanate absorption in the IR-spectrum. The products were precipitated from pentane and subsequently freeze-dried from benzene. The signals of the morpholine group are between 3.0 and 4.0 ppm. We used the integrals of these protons and the sum of the other protons to calculate the copolymer composition as given in Table 1. In carbon NMR (Fig. 2) the signals of the methyl carbons are at 17.7 for the ester and at 19.6 ppm for the isocyanate. At 27.7 ppm is the resonance of the methyl carbons of the *tert*-butyl group. The quaternary carbons have signals at 43.8 ppm (−C−NH) and 80.7 ppm ($-C(CH_3)_3$). The signals of the morpholine ring are at 46.1 ppm (adjacent to the nitrogen atom) and 66.6 ppm (adjacent to the oxygen). The backbone methylene carbons cause a number of signals in the range from 49 to 58 ppm. Finally there are two carbonyl resonances at 156.0 ppm (urea carbonyl) and 177.2 ppm (ester carbonyl).

In experiment **8** conversion was 21% and thus too high for the calculation of reactivity ratios. In experiments **6** and **7** conversion was above 10% so the method introduced by Kelen and Tüdös was used for the calculation of reactivity ratios [11]. For comparison the methods by Joshi and Joshi [12], Kuo and Chen [13] and Fineman and Ross [14] were also used (Table 2). Best standard deviations were obtained by the Kelen–Tüdös and the Joshi–Joshi method. Hence these results are assumed to be the most reliable. The reactivity ratios are 3.48 ± 0.60 for the *tert*-butyl ester and 0.004 ± 0.04 for the isocyanate. We found 'ideal' copolymerisation behaviour with maximum possible 2-propenyl isocyanate content of 50% in the copolymer. Maleic anhydride, the most common reactive monomer in wet-silylation, for copolymerisation with *tert*-butyl methacrylate has reactivity ratios of 2.95 for *tert*-butyl methacrylate and 0.01 for the anhydride [15]. This shows that the new reactive site 2-propenyl isocyanate has almost the same copolymerisation behaviour as maleic anhydride.

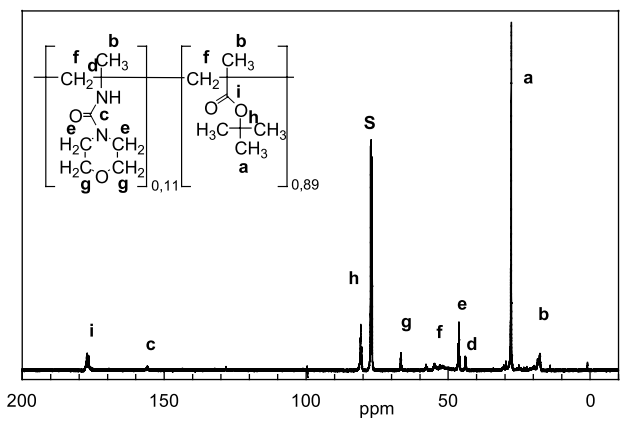



Fig. 2. $^{13}$C NMR-spectrum of poly(*tert*-butyl methacrylate-*co*-2-propenyl isocyanate) **7** reacted with morpholine.

### 3.2. Properties of the copolymers

The molar masses of the copolymers were determined with SEC. The average molar masses are between 1.64 and $4.90 \times 10^3$ g/mol with polydispersities from 1.70 to 2.40. They decrease with increasing 2-propenyl isocyanate content in the monomer feed, which is due to the higher chain transfer activity of the isocyanate as compared to the methacrylate.

The thermal properties of the copolymers were investigated with differential scanning calorimetry (DSC) and thermogravimetry (TGA). The results are included in Table 1. Fig. 3 shows the DSC-traces of two representative copolymers with 21.2 and 29.0% of 2-propenyl isocyanate from which a glass transition temperature and strong endotherms around 255 °C can be seen.

The glass transition temperatures of the copolymers vary from 56 to 114 °C; they increase with increasing *tert*-butyl ester content of the copolymer. The correlation is shown in Fig. 4. Extrapolation gives a glass transition temperature of about 120 °C for poly(*tert*-butyl methacrylate) and of −12 °C for the hypothetical poly(2-propenyl isocyanate). This is in good agreement with the glass transition

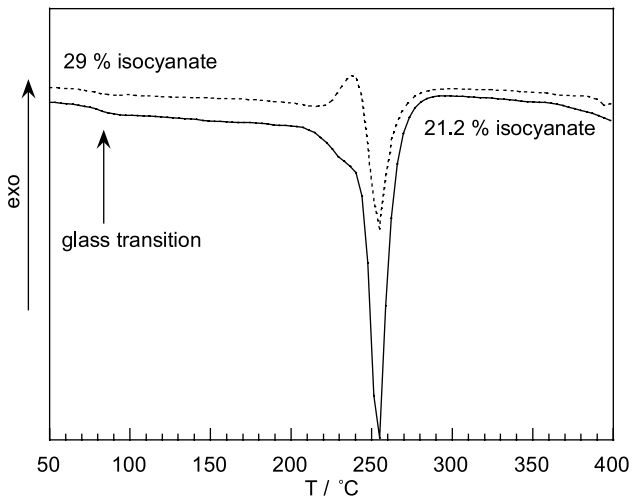



Fig. 3. DSC-traces of copolymers **5** and **6**.

Table 2
Reactivity ratios and standard errors from different methods

| No. | $f_1$ | $F_2$ | | | | |
|---|---|---|---|---|---|---|
| | | Found | Joshi–Joshi; $r_1$ 3.584, $r_2$ 0.005 | Kelen–Tüdös; $r_1$ 3.479, $r_2$ 0.004 | Kuo–Chen; $r_1$ 3.666, $r_2$ 0.132 | Fineman–Ross; $r_1$ 3.610, $r_2$ 0.051 |
| **3** | 0.084 | 0.439 | 0.442 | 0.442 | 0.647 | 0.539 |
| **4** | 0.250 | 0.339 | 0.316 | 0.319 | 0.386 | 0.344 |
| **5** | 0.299 | 0.290 | 0.286 | 0.289 | 0.338 | 0.306 |
| **6** | 0.486 | 0.212 | 0.186 | 0.190 | 0.203 | 0.192 |
| **7** | 0.711 | 0.170 | 0.155 | 0.158 | 0.165 | 0.159 |
| **8** | 0.601 | 0.079 | 0.079 | 0.081 | 0.081 | 0.080 |
| Standard error | | | 0.0169 | 0.0145 | 0.0976 | 0.0465 |

temperature of 118 °C for atactic poly(*tert*-butyl methacrylate) from the literature [16].

In DSC, endo- and exothermal peaks are detected (Fig. 3). The exotherm with a peak-temperature of 234–238 °C is detected in the copolymers with an isocyanate content of 29% or higher. With decreasing isocyanate content the enthalpy of the signal decreases. We assume that the chemical reaction causing this heat flow is present in all samples but is overlapped by the increasing enthalpy of the second signal the peak-temperature of which is roughly constant with 252 °C. This endotherm is caused by the thermal *cis*-elimination reaction of the *tert*-butyl ester as the enthalpy increases with increasing *tert*-butyl ester content.

To analyse the origin of the signal detected in the copolymers with high isocyanate content we tried to correlate polymer composition to mass loss in TGA, which is shown in Fig. 5. From copolymers containing *tert*-butyl methacrylate it is known that the mass loss at elevated temperature can be correlated to the ester content [2]. First reaction is the *cis*-elimination of isobutylene, second is the formation of anhydride from two adjacent acid groups under evaporation of water, a reaction with maximum conversion of 86.5% because of trapped units [1,2]. Fig. 5 shows the experimental values as parabolic curve, it does not fit the linear decrease with decreasing *tert*-butyl ester content as expected (straight line with rhombus).

The experimental values are higher than expected, the largest difference is found for an isocyanate content of about 25%.

This suggests that further reactions take place during heating of the copolymers. Some possible reactions are shown in Scheme 2. The additional reaction is the formation of pyrrolidine-2-one from an isocyanate and an adjacent acid group with elimination of carbon dioxide. Formation of carbon dioxide as side product can also account for the higher mass loss observed in TGA. Calculation of the mass loss assuming that only the reaction of all isocyanate groups with acid groups occurs gives the relationship shown in Fig. 5 as straight line with squares. The theoretical values are higher than the experimental indicating that both reactions of Scheme 2 take place.

To further support this assumption we studied these reactions in bulk as a film and in solution. A film of polymer **3** on a sodium chloride disc was heated in the IR-spectrometer to 210 °C for 2 h. IR-spectra before and after the reaction are shown in Fig. 6. The spectra show a decrease of CH-absorptions at 2977 and 2935 $cm^{-1}$ (loss of *tert*-butyl moieties) and even more pronounced of the NCO-absorption at 2262 $cm^{-1}$. New absorptions at 3540 $cm^{-1}$ from an NH-group and in the carbonyl region appear. The carbonyl band of the *tert*-butyl ester disappears while several new absorptions are to be seen. At 1803 and

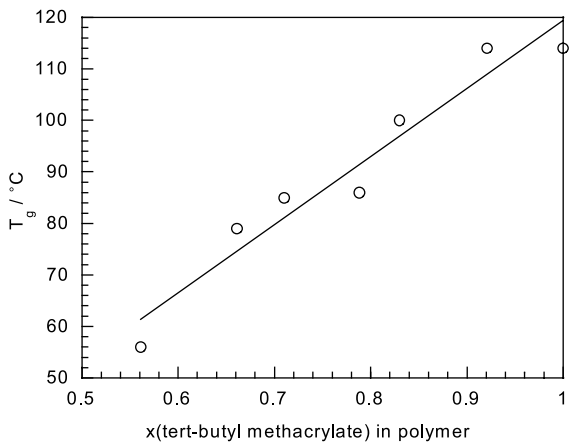



Fig. 4. Glass transition temperature as function of *tert*-butyl methacrylate content of copolymer.

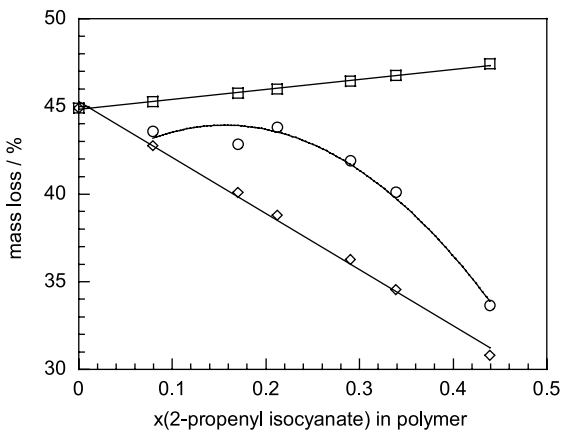
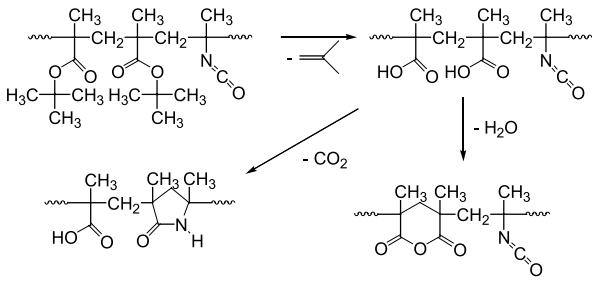



Fig. 5. Mass loss as function of copolymer composition (○ measured; □ calculated including $CO_2$-formation; ◇ calculated without $CO_2$-formation).



Scheme 2.

1759 $cm^{-1}$ there are the two bands from the anhydride groups, the carbonyl absorption at 1718 $cm^{-1}$ can be attributed to the pyrrolidine-2-one.

Thermal reactions of the copolymer in solution were studied with dry diphenylether as solvent at 200 °C for 6 h. In the course of the reaction the polymer precipitated from the solution. It was purified by filtration and subsequent trituration with 200 ml of dry benzene to wash out unmodified polymer. The infrared-spectrum is identical to that from the reaction in film. The NMR-spectra further support the reactions in Scheme 2. In the proton NMR-spectrum the signal of the *tert*-butyl group has disappeared instead a signal of the NH-proton at 3.31 ppm and of the acid proton at 12.72 ppm has appeared. The carbon NMR-spectrum is rather complicated (Fig. 7). Again the signal of the *tert*-butyl group is absent. The spectrum shows the different methyl groups at 16.6 ppm ($H_3C$–C–COOH), 18.6 ppm ($H_3C$–C–CO; pyrrolidine-2-one), 20.1–29 ppm (anhydride), and 30.7 ppm ($H_3C$–C–NH). The methylene absorptions are at 42.9 ppm (anhydride), 44.2 (pyrrolidine-2-one), and 49.0 (polymer backbone). Finally there are the carbonyl absorptions of the anhydride at 172.0 ppm and of pyrrolidine-2-one at 177.8 ppm.

The structure of the polymer obtained by heating poly(*tert*-butyl methacrylate-*co*-2-propenyl isocyanate) to 200 °C is shown in Scheme 3. The polymer is soluble in polar aprotic solvents like dimethyl sulfoxide and dimethyl formamide, acetone and 2-butanone and insoluble in less polar solvents while protic solvents cause ring opening

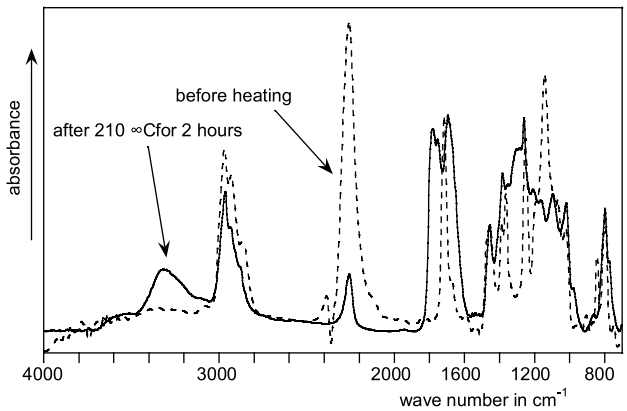



Fig. 6. IR-spectra of poly(*tert*-butyl methacrylate-*co*-2-propenyl isocyanate) before and after heating to 210 °C for 2 h.

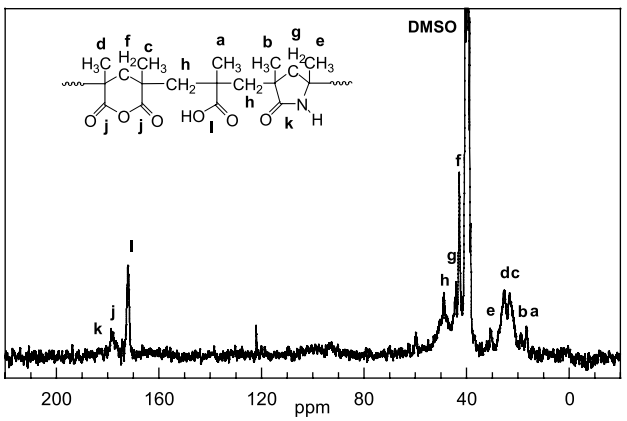



Fig. 7. $^{13}C$ NMR-spectrum of poly(*tert*-butyl methacrylate-*co*-2-propenyl isocyanate) after heating to 210 °C for 2 h.

reactions of the pyrrolidine-2-one and the anhydride. It is remarkable that the two reactions discussed are strongly intramolecular as no insoluble material was formed.

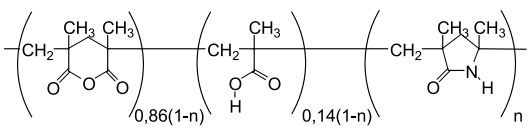
## 4. Conclusions

Copolymerisation of *tert*-butyl methacrylate with 2-propenyl isocyanate has been investigated. The rate of polymerisation increases with increasing *tert*-butyl methacrylate content in the monomer feed. Reactivity ratios were 0.004 for the isocyanate and 3.48 for the *tert*-butyl ester. The reactivity ratios are practically the same as for copolymerisation of maleic anhydride with *tert*-butyl methacrylate.

Conversion of the isocyanate groups to ureas by reaction with morpholine was performed to demonstrate the high reactivity of the copolymers and used to determine composition of the copolymers. Apart from thermal *cis*-elimination of isobutylene from the *tert*-butyl ester group further reactions occur at temperatures around 200 °C. These were identified as formation a six-membered cyclic anhydride accompanied by formation of water, and as a reaction of the isocyanate groups with adjacent acid groups. This reaction leads to formation of a pyrrolidine-2-one and carbon dioxide.

The glass transition temperature of the copolymers increases with increasing *tert*-butyl methacrylate content of the polymer. The molar mass of the polymers decreases with increasing 2-propenyl isocyanate content of the monomer feed due to the higher chain transfer activity of this monomer.

The present study demonstrates that 2-propenyl isocyanate can be used as an alternative reactive species in the




Scheme 3.

wet-silylation reaction photoresist technology, e.g. in the CARL process. Controlled synthesis of copolymers is possible on the basis of the reactivity ratios. Studies of the performance of these copolymers in two layer resists are underway.

## Acknowledgements

The present study was funded by Infineon Technologies AG, MP PMT, Erlangen, Germany.

## References

[1] Grant DH, Grassie N. Trans Faraday Soc 1959;55:1042.
[2] Choi W-J, Kim Y-B, Kwon S-K, Lim K-T, Choi S-K. J Polym Sci, Part A: Polym Chem 1992;30:2143.
[3] Penzel E, Rieger J, Schneider HA. Polymer 1997;38(2):325.
[4] Sebald M, Leuschner R, Sezi R, Ahne H, Birkle S. Proc SPIE 1990; 1262:528.
[5] Kleimann H. Angew Makromol Chem 1981;98:185.
[6] German Patent E 08208 DE; 2001.
[7] Hart R. Bull Soc Chim Belg 1956;65:291.
[8] Mormann W, Grimm A. J Polym Sci, Part A: Polym Chem 1998;36: 611.
[9] Mormann W, Schmalz K. Macromolecules 1994;27:7115.
[10] Kelen T, Tüdös F. J Macromol Sci, Chem 1981;A16(7):1283.
[11] Kelen T, Tüdös F, Földes-Berezsnich T, Turcsany B. J Macromol Sci, Chem 1976;A10(8):1513.
[12] Joshi RM, Joshi SG. J Macromol Sci 1971;A5:1329.
[13] Kuo J-F, Chen C-Y. J Appl Polym Sci 1982;27:2747.
[14] Fineman M, Ross SD. J Polym Sci 1950;5:259.
[15] Ferbitz J, Mormann W. Macromol Symp 2002;181(1):63.
[16] Lee WA. The glass transition temperatures of polymers. In: Bandrup J, Immergut EH, editors. Polymer handbook. New York: Wiley; 1975. p. II-147.