Cyclodextrins in Polymer Synthesis: Two-Step Reaction to Aliphatic Poly(methacrylimide) Foams by Thermal Treatment of Copolymers Obtained from Cyclodextrin Complexes of *tert*-Butyl Methacrylate and Various *N*-Alkyl Methacrylamides

Helmut Ritter,*,† Sabine Schwarz-Barac,† and Peter Stein‡

Institute of Organic and Macromolecular Chemistry II, University of Düsseldorf, Universitätsstrasse 1, 40225 Düsseldorf, Germany, and Röhm GmbH & Co. KG, Kirschenallee, 64293 Darmstadt, Germany

Received July 5, 2002; Revised Manuscript Received November 4, 2002

ABSTRACT: The copolymerization of *tert*-butyl methacrylate **(1)** was carried out with the *N*-alkyl methacrylamides, e.g., *N*-octyl methacrylamide **(2)**, *N*-ethyl methacrylamide **(3)**, *N*-cyclohexyl methacrylamide **(4)**, *N*-benzyl methacrylamide **(5),** and methacrylamide **(6)**. Thermal treatment of these copolymers leads to thermal syn elimination of isobutene and to elimination of water due to the spontaneous imidization reaction. Substituted poly(methacrylimides) were obtained having octyl **(12)**, ethyl **(13)**, cyclohexyl **(14)**, benzyl **(15)**, and hydrogen **(16)** as substituents. The products were obtained as foams. Thermal syn elimination of isobutene and elimination of water were investigated by thermogravimetry. The products contain units of imide, anhydride, amide, and traces of ester. By means of NMR spectroscopy, the content of imide in relation to unreacted amide was calculated. The imide content varies from 44% to 85%. The glass transition temperatures (T_g) of the imides were found to be in the region of 73−165 °C. The molecular weights of the copolymers and the poly(methacrylimides) were analyzed by gel permeation chromatography.

Introduction

Although poly(methacrylates) have found a wide area of practical applications as versatile engineering plastics, they are limited to their high-temperature properties. One possible route to improve the high-temperature properties is to introduce cyclic imide units in the polymers backbone to reduce the mobility of the main chain. This is presently done in industry by a chemical treatment of poly(methacrylates) with amines yielding substituted poly(methacrylimides). The synthesis of poly(methacrylimides) via aminolysis of PMMA with a primary amine in a polymer-analogous reaction had been first proposed by Schröder.[1] He also described the synthesis of poly(methacrylimides) from methacrylamide copolymers via elimination of small molecules.[1]

Poly(methacrylimides) are commercially used as foamed materials. So far, commercial production of poly(methacrylimides) is limited to the substituted derivative poly(*N*-methyl methacrylimide) (PMMI) and the unsubstituted derivative poly(methacrylimide) (PMI). PMMI, a highly distortion-resistant compound which is particularly suitable for injection molding, is obtained directly from poly(methyl methacrylate) via aminolysis with methylamine in an extruder.[1] The success of the preferred technical synthesis of substituted poly(methacrylimides) depends mostly on high pressure. PMI is preferably used for insulation where high thermal stability and low weight are required. This polymer is prepared by an intramolecular cyclization reaction by heating a copolymer of methacrylonitrile and methacrylic acid over a long time period.

To overcome the above-mentioned problems, we were encouraged to develop a new method to synthesize poly(methacrylimides). Regarding our interests to use cyclodextrins in polymer synthesis in aqueous media,[2−8] we focused our attention on the copolymerization of water-soluble cyclodextrin-complexed *tert*-butyl methacrylate and various *N*-alkyl methacrylamides. An economical synthesis of aliphatic N-substituted poly(methacrylimides) via thermal treatment of *tert*-butyl methacrylate/N-substituted methacrylamide copolymers has not been reported so far.

We hereby describe in the present paper the copolymerization of corresponding cyclodextrin complexes of the required monomers. We also report the thermal treatment of the obtained copolymers.

Experimental Section

Materials. *tert*-Butyl methacrylate **(1)** and methacrylamide **(6)** were obtained by Sigma-Aldrich-Chemie GmbH, Taufkirchen, FRG. *tert*-Butyl methacrylate was distilled under reduced pressure. *N*-Ethyl methacrylamide **(3)**, *N*-cyclohexyl methacrylamide **(4),** and *N*-benzyl methacrylamide **(5)** were obtained from ABCR GmbH & Co., A better Choice for Research Chemicals, Karlsruhe, FRG. Octylamine, methacryloyl chloride, and triethylamine were purchased from Acros, Organics N.V./S.A., Geel. The methylated β-cyclodextrin (Me-β-CD) was obtained from Wacker-Chemie GmbH, Burghausen, FRG, with an average degree of methylation of about 1.8 per glucose unit (CAVASOL W7M, technical grade). Potassium persulfate and sodium disulfite were obtained from Acros, Organics N.V./S.A., Geel, Belgium. 2,2′-Azobis(amidinopropane) dihydrochloride (AAP) was obtained from Wako Chemicals GmbH, Kastellaun, FRG. Demineralized water was boiled before use. Chloroform-d_1 (99.8 atom % deuterium) and dimethyl-d_6 sulfoxide (99.8 atom % deuterium) were purchased from Deutero GmbH, Kastellaun, FRG.

The ^{1}H NMR spectra of the polymers were recorded on a Bruker AC 200. HPLC measurements were performed by the use of a Biotec 525 system with a Biotec 540 diode array detector and a Knaur RI detector. SEC measurements were performed with a setup of the company PSS (Polymer Stan-

---

† University of Düsseldorf.

‡ Röhm GmbH & Co. KG.

* Corresponding author: e-mail h.ritter@uni-duesseldorf.de.

10.1021/ma021055j CCC: $25.00

Table 1. Copolymerization Data of Polymers 7−11

polymer	comonomer	mon[a] [mmol]	initiator	T [°C]	molar ratio mon/Me-β-CD	reaction time [h]	M_w [g mol^{-1}]	M_n [g mol^{-1}]	P_n[b]	conv [wt %]	amide content [mol %]
7a	**2**	4.80	AAP	50	1:1.5	75	59 300	28 400	2.1	22	49
7b	**2**	4.80	AAP	50	1:1.5	2	62 900	26 300	2.4	24	47
7c	**2**	4.80	$K_2S_2O_8$	25	1:1.5	2	66 800	26 200	2.6	57	44
7d	**2**	4.80	$K_2S_2O_8$	50	1:1.5	3.2	33 000	14 000	2.4	51	57
7e	**2**	4.80	$K_2S_2O_8$	50	1:1.5	3	42 100	13 900	3.0	58	51
7f	**2**	48.02	$K_2S_2O_8$	50	1:1.5	3.2	328 200	65 600	5.0	56	55
8a	**3**	4.80	$K_2S_2O_8$	50	1:1.5	4	16 000	8 700	1.9	63	45
8b	**3**	35.34	$K_2S_2O_8$	50	1:1.0	4	88 000	22 000	4.0	84	43
9	**4**	4.80	$K_2S_2O_8$	50	1:1.5	3	50 200	14 000	3.6	50	29
10	**5**	4.80	$K_2S_2O_8$	50	1:1.5	3	60 400	13 200	4.6	67	29
11	**6**	48.00	$K_2S_2O_8$	50	1:1.5	4	12 400	6 300	2.0	63	50

[a] Quantity of substance of comonomer. [b] $P_n = M_w/M_n$.

dards Service GmbH, Mainz, FRG) with dimethylformamide as eluent at 25 °C and toluene as internal standard. Calibration was done with polystyrene standards (PSS) ranging from 374 to 1 000 000 g/mol (flow rate of 1 mL/min). 150 μL of a 0.125 wt % polymer solution was introduced into a column combination consisting of a Hema 10 μm precolumn and a set of Hema 10 μm as analytical columns (40, 100, 3000 Å porosity). Detection of the signals was performed with a TSP UV2000 UV−vis detector (254 nm) and a modified Knauer RI detector. UV measurements were conducted on an Unicam UV 540 system. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC7. Thermogravimetric measurements (10 K/min) were generously performed by the service for thermoanalysis of Röhm GmbH & Co. KG on a TA-Instrument TGA 2950. The FT-IR spectra were recorded on a Nicolet FTIR-5 SXB, ATR unit. SEM was performed by the Institute of Physical Chemistry and Electrochemistry at the University of Düsseldorf, with a Philipps XL30-ESEM electron microscope.

Synthesis of *N*-Octyl Methacrylamide (2). Methacryloyl chloride (1.25 g, 12.0 mmol) dissolved in dry dichloromethane (10 mL) was added dropwise to a cooled mixture (0 °C) of octylamine (1.55 g, 12.0 mmol) and triethylamine (4.08 g, 40.0 mmol) in dry dichloromethane (60 mL). After warming to ambient temperature the mixture was stirred for 20 h. The reaction mixture was poured into a 250 mL mixture of dichloromethane and water (1.5:1, vol:vol). The solution was washed two times with 100 mL of 2 M hydrochloric acid and two times with 100 mL of deionized water. The organic phase was dried over $MgSO_4$. Finally, the organic phase was evaporated, and **2** was obtained as a viscous pale yellow liquid.

Yield 4.69 g, 99%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 5.90 (br s, $-NH-$); 5.61, 5.24 (s, 2H, $CH_2{=}C(CH_3)-$); 3.22 (q, J = 7.2 Hz, 2H, $-NH-CH_2-$); 1.92 (s, 3H, $CH_2{=}C(CH_3)-$); 1.49 (m, J = 7.0 Hz, 2H, $-NH-CH_2-CH_2-$); 1.21 (s, 10H, $-(CH_2)_5$); 0.84 (t, J = 6.5 Hz, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] 168.4 ($\rangle C{=}O$); 140.1 ($H_2C{=}C-$); 119.1 ($H_2C{=}C\langle$); 40.0 ($-NH-CH_2-$); 31.7, 29.5, 29.2, 26.9, 22.6 ($-NH-CH_2-(CH_2)_6-$); 18.7 ($CH_2{=}C(CH_3)-$); 14.0 ($-CH_3$). FT-IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3340 (NH stretching); 2960, 2930, 2860 ($\nu_{as,s}$ CH stretching aliphatic); 1660 (C=O stretching, amide I); 1620 (C=C); 1540 (NH bending, amide II); 1455 (δ_{as} CH aliphatic); 1375 (sym δ_s CH_3). On the basis of NMR results, the product was pure and a distillation was not necessary.

Complexation of Monomers and Copolymerization. A three-necked flask, fitted with stirrer and nitrogen inlet, was evacuated and filled with nitrogen three times. The following monomers were complexed: *tert*-butyl methacrylate **(1),** *N*-octyl methacrylamide **(2)**, *N*-ethyl methacrylamide **(3)**, *N*-cyclohexyl methacrylamide **(4),** *N*-benzyl methacrylamide **(5),** and methacrylamide **(6)**. As an example, only one of the copolymerizations is described here in detail. The conditions of all other copolymerizations are given in Table 1. To carry out the copolymerization of the complexed monomers in a molar ratio of 1:1.5 (monomer: Me-β-CD), 18.88 g (14.40 mmol) of Me-β-CD was dissolved in 63 mL of deaerated water. Then 0.68 g (4.80 mmol) of *tert*-butyl methacrylate **(1)** and 0.54 g (4.80 mmol) of **(3)** were added while stirring and passing a gentle stream of nitrogen through the reaction vessel. The mixture was stirred under a nitrogen atmosphere for 20 min, yielding a clear colorless solution of the complexed monomers **(1a, 3a)**. The solution was heated to 50 °C. To start the copolymerization, freshly prepared solutions of the initiators $K_2S_2O_8$ and $Na_2S_2O_5$ (or AAP respective) were added with stirring. The polymerization was terminated by cooling the reaction mixtures in an ice bath and passing air through the reaction mixture. The precipitated polymer was filtered off and washed with 3 × 20 mL of water. The obtained colorless polymeric product still contained a small amount of Me-β-CD according to NMR and IR spectroscopy. To remove residual Me-β-CD, the copolymer was extracted again with water. The copolymer was finally dried in high vacuum. The copolymer was soluble in dimethyl sulfoxide and dimethylformamide. Less than 4 mol % of Me-β-CD remained in the products. With the exception of the copolymer based on monomer **6**, all polymers precipitated during the polymerization. We determined the reactivity ratio for the copolymerization of **1** and **3** in the presence of Me-β-CD by determination of the remaining monomer concentration by HPLC: $r_{(1)} = 0.48$, $r_{(3)} = 0.34$. The reactivity ratios were derived using the method of Kelen and Tüdös.[9−11] We observed a tendency toward a nonideal azeotropic statistic copolymerization. As a typical example, we present the characteristical data of poly(*tert*-butyl methacrylate-*co*-*N*-ethylmethacrylamide) **(8)**.

Poly(tert-butyl methacrylate-co-N-ethylmethacrylamide) ***(8)***. ^{1}H NMR (DMSO-d_6, 200 MHz): δ [ppm] 7.39 (br s, $-NH-$); 3.16−2.71 (br s, $-NH-CH_2-$); 2.36−1.60 ($-CH_2-$ chain); 1.60−1.18 ($-(C(CH_3)_3)-$); 1.18−0.23 ($-CH_3$). FT-IR (ATR, ν [cm^{-1}]): 3471 (NH stretching); 2975, 2933 ($\nu_{as,s}$ CH stretching aliphatic); 1717 (C=O stretching); 1645 (C=O stretching, amide I); 1518 (NH bending, amide II); 1479, 1457 (δ_{as} CH aliphatic); 1392, 1367 (δ_s $C(CH_3)_3$).

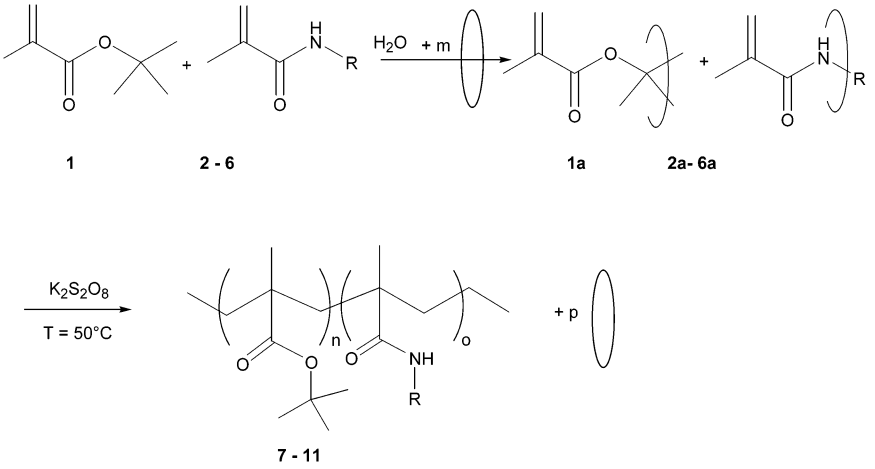
Results and Discussion

For the preparation of thermosensitive copolymers the methacrylamides *N*-octyl methacrylamide **(2)**, *N*-ethyl methacrylamide **(3)**, *N*-cyclohexyl methacrylamide **(4)**, *N*-benzyl methacrylamide **(5),** and methacrylamide **(6)** were complexed with dimethylated β-cyclodextrin (Me-β-CD), yielding the water-soluble complexes **2a**, **3a**, **4a**, **5a**, and **6a**. The complexation of *tert*-butyl methacrylate **(1)** was carried out with Me-β-CD, yielding a clearly water-soluble complex **(1a)** that was used as a common comonomer.

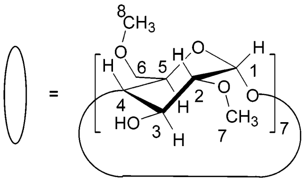
It is relevant to consider the water solubility of the different monomers **1**−**6**. Depending on the water solubility of these monomers, the polymerization may take place also in the water phase without prior complexation leading to coagulation of the polymers. In this case two polymerization mechanisms may occur side by side.

For example, at room temperature (20 °C) the homopolymerization of **1a** takes place readily, but without

Scheme 1. Complexation of Different Monomers 1–6 and Copolymerization of Complexed Monomers 1a–6a to Copolymers 7–11



R	monomer	complex	polymer
-octyl	2	2a	7
-ethyl	3	3a	8
-cyclohexyl	4	4a	9
-benzyl	5	5a	10
-H	6	6a	11



cyclodextrin no polymerization occurs under similar conditions.[12] This implies that the polymerization starts with the molecular dispersed complexed monomer **(1a)** and not from the fraction of the partially dissolved free monomer **(1)**. At higher temperatures (80 °C), **1** as well as **1a** homopolymerizes readily, probably due to the higher water solubility at elevated temperatures.[12]

The water solubility of **1** was determined to 0.34 g/L by means of UV spectroscopy. The monomers **3** and **6** (202 g/L[13]) are quite soluble in water, whereas **2**, **4**, and **5** are nearly insoluble in water.

Synthesis of Copolymers. The copolymerization of different Me-β-CD-complexed *N*-methacrylamides **2a–6a** with complexed *tert*-butyl methacrylate **(1a)** was carried out in water as reaction medium (Scheme 1). Upon polymerization the polymer precipitated from the solution, leading to a heterogeneous system.

Generally, the polymerization using the azo-initiator AAP resulted in relatively low yields **(7a, 7b)** (Table 1). We thus applied the redox initiator system potassium persulfate/sodium disulfite. The content of amide in the copolymers **7a–7f** (Table 1) differs from 44 to 55%. By copolymerization of **1** and **2** in water in the presence of cyclodextrin, it is possible to obtain a copolymer with an ester-to-amide proportion of approximately 1:1. Regarding yield and molecular weight, the polymerizations have to be optimized.

Considering the copolymers **8a** and **8b** (Table 1), it is obvious that the yield increases by a lower cyclodextrin content and a scaling-up. The lower content of cyclodextrin is necessary due to the higher water solubility of *N*-ethyl methacrylamide **(3)** in comparison with e.g. *N*-octyl methacrylamide **(2)**. The content of amide varies from 43 to 45 mol %. Regarding the copolymerizations of the monomers **4** and **5**, the content of amide in copolymers **9** and **10** (Table 1) is significantly lower (30 mol %). With the water-soluble monomer **6** we obtained also a copolymer **11** (Table 1) with a molar ratio of ester to amide of 1:1. Because of the significant water solubility of this copolymer **11**, the polymerization did not proceed as a precipitation polymerization. For the copolymers **7**, **8**, and **11** the content of incorporated sequences of **1** correlates with the initial monomer concentration, although the conversion is only in the region of 50–67%.

Thermal Modification. The thermal treatment of the copolymers **7–11** leads to thermal syn elimination of isobutene and to elimination of water due to the imidization reaction (Scheme 2).

Figure 1 illustrates the appearance of original copolymer and thermolyzed product.

The pyrolyzed polymers contain units of imide, anhydride, amide, and traces of ester. With continuous thermal treatment adjacent units of amide and acid react to form imide units. By means of thermogravimetry, observation of elimination is enabled. In some cases we observed three steps of mass loss; in other cases syn elimination and imidization occur simultaneously. Thermogravimetric analysis of copolymer **7c** (Table 1) reveals three distinctive steps as can be seen from the derivation. The first corresponds to the mass change in the syn elimination, and the second corresponds to the imidization reaction, whereas the third step indicates partial degradation of the product.

For poly(alkyl methacrylates) with substituents like *tert*-butyl, isopropyl, and *sec*-butyl, thermal syn elimination is favored to depolymerization. The formation of methacrylic acid and/or methacrylic anhydride units normally prevents a significant depolymerization, and thus the breakdown to monomers[14] and oligomers is reduced.

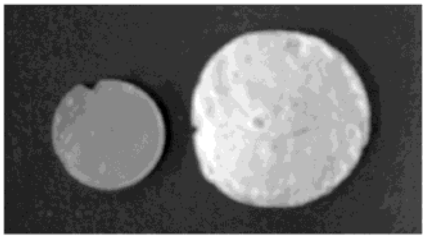


Figure 1. Picture of copolymer **8b** (Table 1) and thermolyzed product **13i** (Table 3).

Scheme 2. Synthesis of Poly(methacrylimides) 12−16 by Thermal Treatment of the Copolymers 7−11

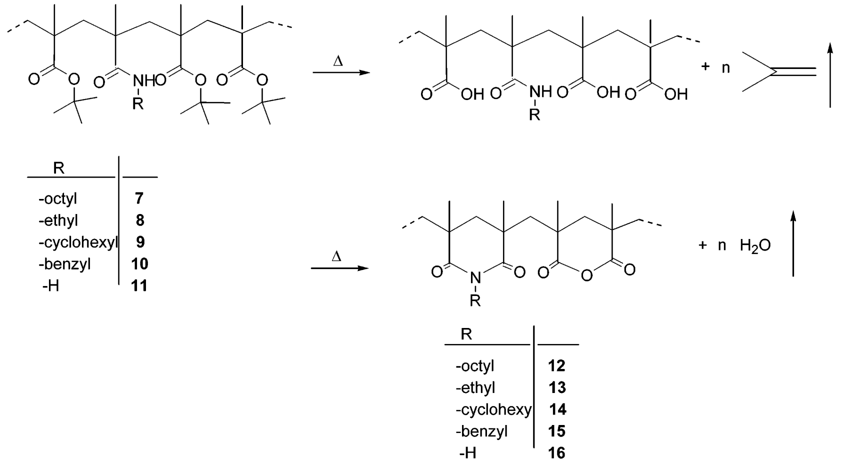


Table 2. Results of Thermogravimetric Analysis

polymer	mass loss [wt %]	$T_d{}^a$ [°C]	polymer	mass loss [wt %]	$T_d{}^a$ [°C]
7c	50	375	**8b**	32	328
7d	31	300	**9**	42	327
7f	35	309	**10**	37	310

[a] T_d = temperature of starting decomposition.

Depending on the incorporated units of *tert*-butyl methacrylate, the polymers **7c, 7d, 7f, 8b, 9**, and **10** exhibit various losses of mass. Table 2 presents the results of the thermogravimetric analysis. The elimination of water due to imidization is superimposed by the elimination of water due to formation of anhydride functions. The nonnegligible part of anhydride formation is visible in the IR spectra. In comparison with the theoretical expected mass losses, all experimental values are slightly higher. As mentioned above, partial depolymerization may be a factor.

The thermal decomposition of the copolymers starts in general from 300 to 375 °C. The thermal degradation of Me-β-CD begins at 240 °C. Depending on the conditions of thermolysis, the products still contain cyclodextrin. The color of the different poly(methacrylamides) (yellow to brown) is not due to cyclodextrin. The thermolysis of a copolymer synthesized without cyclodextrin led to a colored product, too.

Because of the elimination of isobutene and water, the poly(methacrylimides) were obtained as foams. A foaming of the polymer is observed in the shape of a block. When the thermal treatment is performed in thin films, the foaming agent diffuses.[15] Figure 3 shows the SEM of a fracture surface of the broken-up foam of poly(*N*-ethylmethacrylimide) **(14d)** (Table 1) As can be seen, the cells of the foam are of different sizes. Most of the cells are closed. We determined a density of 300 kg/m^3.

Characteristics of Poly(methacrylimides) 12−16. The thermolysis conditions, the molecular weights, the amide/imide contents, and the glass transition temperatures are shown in Table 3. We calculated the degree of imidization by considering the integrated resonances of amide and imide protons ($-NH-CH_2-$ and $\rangle N-CH_2-$). A calculation of the molar content of amide, imide, ester, and anhydride is not possible.

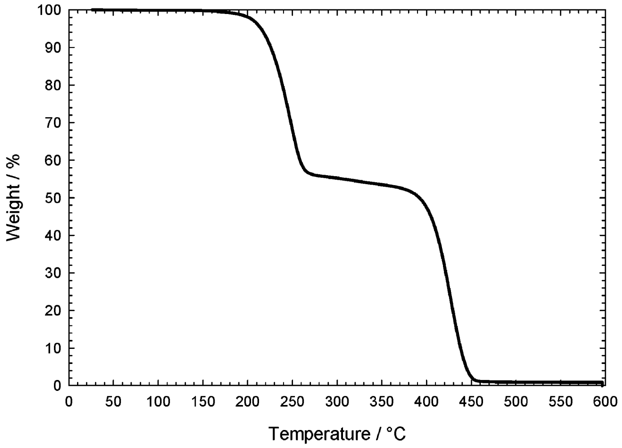


Figure 2. Thermogravimetry: thermogram of poly(*tert*-butyl methacrylate-*co*-*N*-octyl methacrylamide) **(7c)** (Table 1).

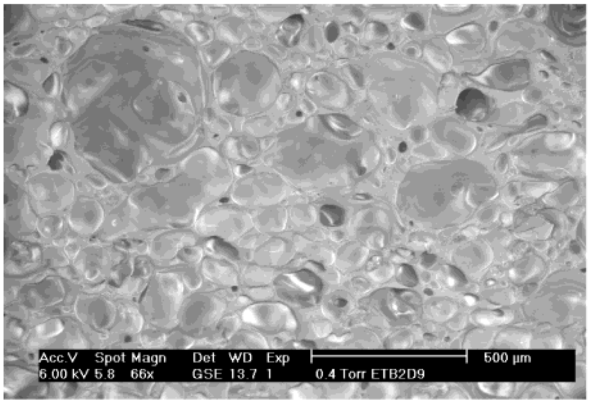


Figure 3. SEM of fracture surface of the broken-up foam of poly(*N*-ethyl methacrylimide) **(14d)**.

Because of the coupling of the carbonyl stretching vibrations in the system $O{=}C-N-C{=}O$, we observe, depending on the substituent, a frequency separation from 40 up to 70 cm^{-1}.[16] So for the substituents ethyl and octyl a separation of 55 and 56 cm^{-1} was observed. For the bulkier substituents cyclohexyl and benzyl we obtained a separation of 59 cm^{-1}. For the substituent hydrogen we can observe no frequency separation. There is always formation of anhydride (1804, 1756 cm^{-1}). Unreacted amide is visible at 1525 cm^{-1}. According to IR spectroscopy, it was revealed that the content of anhydride is nonnegligible, especially for the polymers **14b** (Table 3), **15b,** and **15c** (Table 3). On account of the relatively low amide content of the polymers **9** and **10** (29%) (Table 1), we expected this. Steric factors play an important role in the imidization reaction.[17]

Table 3. Thermolysis Parameter, Molecular Weight, Imide-content and T_g of Poly(N-octylmethacrylimides) (12), Poly(*N*-ethylmethacrylimides) (13), Poly(N-cyclohexylmethacrylimides) (14), Poly(N-benzylmethacrylimides) (15) and of Poly(methacrylimides) (16)

polymer	T [°C]	time [min]	M_w [g mol^{-1}]	M_n [g mol^{-1}]	P_D	imide [%]	T_g [°C]
12a	300	95	40 000	15 700	2.6	67	74
12b	260	180	126 000	31 200	4.0	63	73
13a	230	222	88 000	22 000	4.0	41	129
13b	240	141	67 000	18 000	3.7	88	145
13c	240	260	33 300	11 900	2.8	80	146
13d	250	122	98 000	19 000	5.2	86	146
13e	250	260	77 600	18 000	4.3	91	164
13f	250	309	75 000	20 000	3.8	83	165
13g	260	80	42 100	11 900	3.5	87	*a*
13h	280	79	67 800	21 800	3.1	*a*	144
14a	220	245	41 500	10 100	4.1	28	*a*
14b	230	470	66 300	12 000	5.6	32	134
14c	250	90	88 700	15 200	5.8	33	124
15a	220	60	30 600	8 000	3.8	68	82
15b	250	15	63 800	14 000	4.6	91	*a*
15c	260	145	105 100	14 000	7.5	83	120
16a	220	92	23 000	12 400	1.9	*a*	163
16b	250	56	36 800	11 700	3.1	*a*	153

[a] Data not available.

Matsumoto et al. observed for films of nonaromatic polyimides a small absorption at 280 nm due to carbonyl n → π^* transition.[18] In accordance with these investigations, we found absorptions for the polymers **12**−**16** (Table 3) in the region of 271−280 nm. The original copolymers **7**−**11** (Table 1) showed no absorption in this region.

Thermal Behavior of the Synthesized Poly(methacrylimides) 12−16. The glass transition temperatures for the copolymers are apparently lower than for the thermolyzed products, with exception of the systems with the substituents octyl and benzyl. The glass transition temperatures of the homopolymers poly(*tert*-butyl methacrylate) and poly(*N*-octyl methacrylamide) polymerized in the same manner have been determined as 114 and 71 °C, respectively. The glass transition temperatures of poly(*N*-ethyl methacrylimides) **13a**−**13h** vary from 129 to 165 °C, depending on the degree of imidization. For the substituent hydrogen T_g achieves 153 and 165 °C, respectively.

Conclusions

We realized the copolymerization of several *N*-alkyl methacrylamides with *tert*-butyl methacrylate in water in the presence of dimethyl-β-cyclodextrin. In this study different substituted poly(methacrylimides) were synthesized by thermal treatment of these copolymers. This method offers a simple way to vary the substituent. In comparison with the so far known synthesis of poly(methacrylimides), the here described thermal treatment of the copolymers possesses the following advantages:

The synthesis of the copolymers occurs in the absence of organic solvents, and a recycling of the cyclodextrin solution is possible. The process can be considered as environment-friendly and ecologically desirable. The elimination of isobutene and the imidization are performed under normal pressures of nitrogen and without any solvents. The formation of isobutene as foaming agent takes place by a chemical reaction. To regulate the porosity, additional foaming agents like azodicarbonamide or urea can be added. In future investigations the use of α-cyclodextrin or other cyclodextrin derivatives will be considered.

Acknowledgment. Financial and technical support of this study by Röhm (Degussa) is gratefully acknowledged. The results of this study are registered as a patent (No. 10150484.5).

References and Notes

(1) Schröder, G. *Makromol. Chem.* **1966,** *96*, 227.
(2) Casper, P.; Glöckner, P.; Ritter, H. *Macromolecules* **2000**, *33*, 4361.
(3) Storsberg, J.; Ritter, H. *Macromol. Rapid Commun.* **2000**, *21*, 236.
(4) Glöckner, P.; Ritter, H. *Macromol. Rapid Commun.* **1999**, *20*, 602.
(5) Glöckner, P.; Metz, N.; Ritter, H. *Macromolecules* **2000**, *33*, 4288.
(6) Glöckner, P.; Ritter, H. *Macromol. Chem. Phys.* **2000**, *201*, 2455.
(7) Bernhardt, S.; Glöckner, P.; Theis, A.; Ritter, H. *Macromolecules* **2001**, *34*, 1647.
(8) Bernhardt, S.; Glöckner, P.; Ritter, H. *Polym. Bull.* **2001**, *46*, 153.
(9) Kelen, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1.
(10) Kelen, T.; Tüdös, F.; Turcsányi, B. *Polym. Bull.* **1980**, *2*, 71.
(11) Kelen, T.; Tüdös, F.; Braun, D.; Czerwinski, W. K. *Makromol. Chem.* **1990**, *191*, 1863.
(12) Schwarz-Barać, S.; Ritter, H., submitted for publication.
(13) Catalogue Sigma-Aldrich Chemie GmbH, Taufkirchen, FRG, 2000.
(14) Scott, G. *Polymer Degradation and Stabilisation, 1. Polymers and Polymerization*; University Press: Cambridge, GB, 1985.
(15) Ganzler, W.; Huch, P.; Metzger, W.; Schröder, G. *Angew. Makromol. Chem.* **1970**, *11*, 91−108.
(16) Hargreaves, M. K.; Pritchard, J. G.; Dave, H. R. *Chem. Rev.* **1970**, *70*, 439.
(17) Belina, K. *J. Therm. Anal.* **1997**, *50*, 655.
(18) Matsumoto, T. *Macromolecules* **1999**, *32*, 4933.

MA021055J