Synthesis and Rheological Behavior of Cross-Linkable Poly[*N*-(methacryl-2-ethyl)-*N*′-(3-amino(1,2,4-triazole-2-yl))urea-*co*-methyl methacrylate]

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ABSTRACT: A copolymer poly[*N*-(methacryl-2-ethyl)-*N*′-(3-amino(1,2,4-triazole-2-yl) urea)-*co*-methyl methacrylate] (**1**) with a low $\bar{M}_n$ value of about 1300 was prepared via free radical polymerization from the corresponding monomers *N*-methacrylethyl-*N*′-triazoyl urea (**2**) and methyl methacrylate (**3**). The complex viscosity of a solution of **1** in *N*-methyl pyrrolidone decreases with increasing temperature up to 32 °C at the beginning and then passes a minimum at 38 °C. At higher temperatures of about 53 °C, it decreases again. DSC measurements of this solution indicates phase transitions because of two endothermic signals from 32 to 44 °C and from 53 to 74 °C. Furthermore, the copolymer **1** starts to cross-link rapidly above 130 °C. The mechanism of this cross-linking reaction is discussed with respect to a back-formation of isocyanate intermediate that reacts with nucleophiles.

Introduction

In general, hydrogen bonds are important in the formation of highly organized supramolecular structures in many biopolymers such as proteins or ,e.g., in the double helix of DNA.[1−3] Additionally, many publications are focused on the synthesis of artificial polymers bearing functional moieties that are able to build up several kinds of hydrogen bonds, e.g., amides, carbamates, urea derivates, or simply carboxylic acids.[4−7] In this connection, it has to be pointed out that the typical mechanical behavior of linear polyamides and polycarbamates is a result of the more or less regularly located hydrogen bonds that strongly improve the intermolecular interactions.

On the basis of our interest in preparation of various polymers bearing functionalized side groups, we were encouraged to synthesize a new type of methacrylate polymer containing a special kind of a hydrogen bond forming moiety based on 3-amino-1,2,4-triazole. To evaluate these intermolecular interactions, we were also interested in the crystal structure of the monomer and in the rheological behavior of the corresponding polymer in solution.

Results and Discussion

Poly[*N*-(methacryl-2-ethyl)-*N*′-(3-amino(1,2,4-triazole-2-yl)urea)-*co*-methyl methacrylate] (**1**) was prepared from the monomers (methacryl-2-ethyl)-*N*′-(3-amino-(1,2,4-triazole-2-yl))urea (**2**) and methyl methacrylate (**3**).

Monomer **2** was obtained simply by reaction of 2-isocyanatoethyl methacrylate (**4**) with 3-amino-1,2,4-triazole (**5**) in the presence of catalytic amounts of dibutyl tindilaurate (DBTL) in dimethylformamide (DMF) as solvent (Scheme 1). It is interesting to note that the nitrogen of the triazole-ring preferably reacts with the isocyanate instead of the primary amino group. The X-ray structure of **2** clearly shows strong intramolecular hydrogen bonds between the amidic N−H group of the urea moiety (N8−H) and the nitrogen (N5) and, in addition between the C═O of the urea moiety (O7) and the primary amino group (N17−H). The relative short bond lengths of these hydrogen bonds of 2.1 and 2.15 Å, respectively, support the postulated high stability of this interaction and therefore stabilizes a planar structure of the triazoyl ring in relation to the urea moiety. There are also two complementary intermolecular hydrogen bonds formed between the primary amino group and a nitrogen of the heterocyclic ring (N17−H···N3b) (2.1 Å) (Figure 1). This structure could be correlated to the ^{1}H NMR spectra measured in dependence on the concentration. We found in CDCl$_3$ solution that the chemical shift of the peak of the NH group involved in intramolecular hydrogen bonds does not depend on the concentration ($\Delta\delta_{max} = 0.03$ ppm). In contrast, the signal of the NH group that is responsible for the intermolecular hydrogen bond depends strongly on the concentration of **2**. Increasing the concentration of **2** leads to a significant shift of the chemical shift to lower field. The maximal difference of the chemical shift between the highest and lowest concentration is of about $\Delta\delta_{max} \approx 0.30$ ppm. This result points out that the structure in solution is similar to the crystal structure.

Monomer **2** and methyl methacrylate (**3**) (molar ratio 1:5) were copolymerized in DMF as solvent in the presence of 8 mol % of azoisobutyro nitrile as initiator. DMF was used due to its very small chain transfer constant. The molar ratio of incorporated monomers **2** and **3** in copolymer was determined by ^{1}H NMR spectroscopy and, according to the integrated signals at 4.13 ppm ($\mathrm{OC}H_2\mathrm{CH_2NH}$) and 4.40−3.10 ppm ($\mathrm{OC}H_3$) it was found to be around 1:5.5. The molecular weight ($\bar{M}_n$) was about 1300 determined by gel permeation chromatography (GPC) with polystyrene as standard. We wanted

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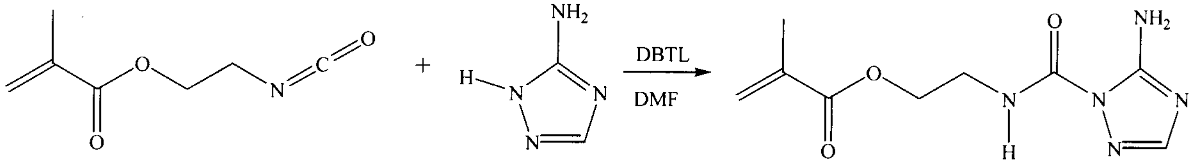
Scheme 1. Synthesis of (*N*-Methacrylethyl-*N*′-triazoyl)urea (2)



4 **5** **2**

to study the viscosity behavior caused by hydrogen-bonding interactions. In this connection the rather low $\bar{M}_n$ of about 1300 was required to avoid polymer–polymer interactions such as entanglements.

For characterization of the rheological behavior, copolymer **1** was dissolved in *N*-methylpyrollidone (N-MP) (50 wt %) and the complex viscosity ($|\eta^*|$) was investigated in dependence on the temperature, which is shown in Figure 2.

Between 20 and 32 °C, $|\eta^*|$ decreases significantly. After a minimum between 32 and 38 °C, there is an increasing of the complex viscosity, and finally, after a maximum at about 53 °C, the complex viscosity decreases again, but the slope is not as high as in the first range.

According to turbidity measurements in dependence on temperature dissolving or precipitation effects are not visible. The DSC measurement of the solution of **1** indicates the existence of an endothermal phase transition between 32 and 44 °C and in addition a further weaker phase transition between 53 and 74 °C. Obviously, these phase transitions seems to correlate with this unusual rheological behavior, as described above.

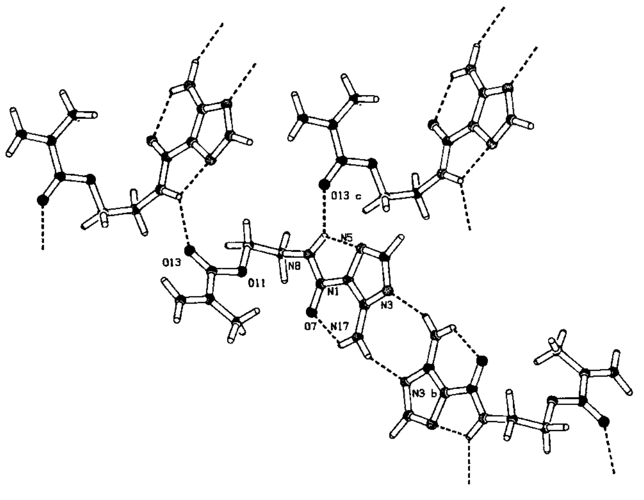


Figure 1. X-ray structure of (*N*-methacrylethyl-*N*′-triazoyl)urea (**2**)

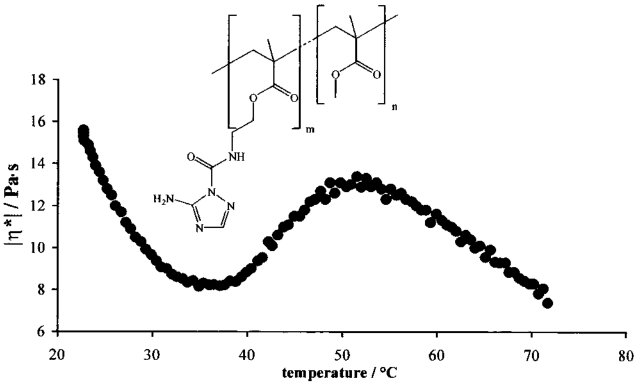


Figure 2. Complex viscosity $|\eta^*|$ [Pa·s] vs temperature [°C] (20–70 °C) of **1** (50 wt % in *N*-methyl pyrrolidone; oscillating measurement, 5 K·min^{-1}, frequency, 1 s^{-1})

Furthermore, the complex viscosity of the solution of **1** increases strongly above a temperature of about 130 °C yielding a cross-linked gel (Figure 4). It is well-known from the literature that the formation of urea derivatives is reversible to build isocyanates. In particular, triazole- or ϵ-caprolactam are similar to 3-amino-1,2,4-triazole. According to model studies, we found a back-formation of the isocyanate, and therefore, this isocyanate moiety reacts at higher temperatures intermolecularly with a primary amino group or with one of the NH groups of urea function (Scheme 2).

For a better understanding of this cross-linking reaction, a low molecular model substance (**7**) was synthesized from aminotriazole (**5**) and ethyl isocyanate (**6**) (Scheme 3).

The (aminotriazolyl)ethyl))urea (**7**) was heated to 130 °C in the presence of benzylamine (**12**). According to mass spectrometry we found aminotriazole, (benzylethyl)urea (**10**), and, in addition, dibenzylurea (**11**). The absorption of the free isocyanate was found at 2250 cm^{-1} in the FT-IR spectrum.

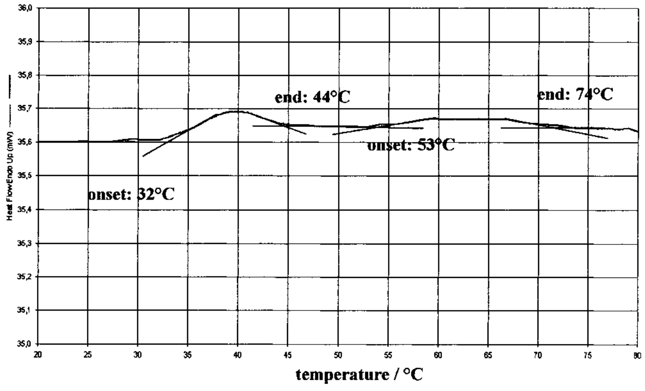


Figure 3. DSC diagram [°C] of **1** (50 wt % in *N*-methyl pyrrolidone; heating rate, 30K·min^{-1}).

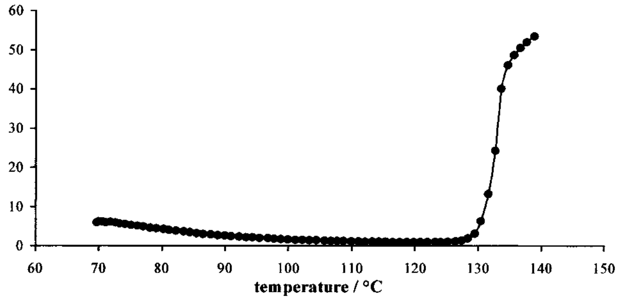
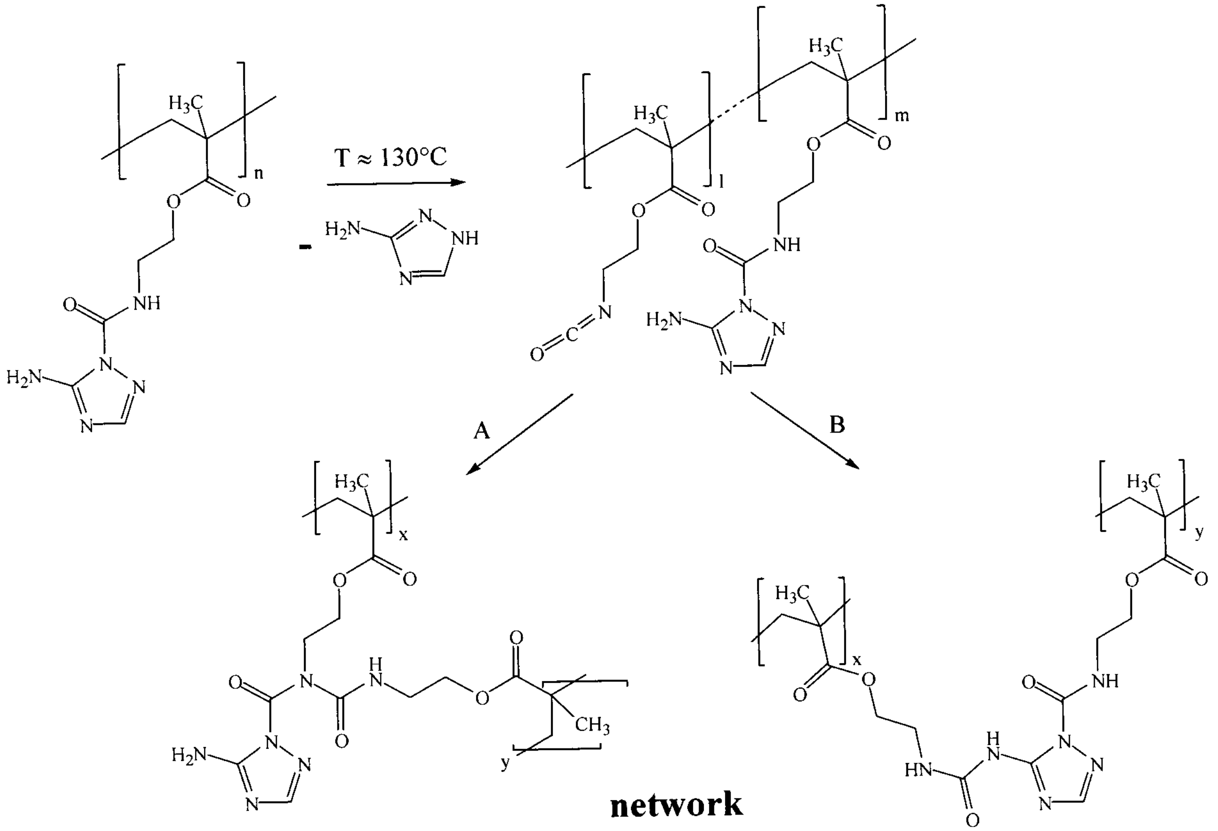
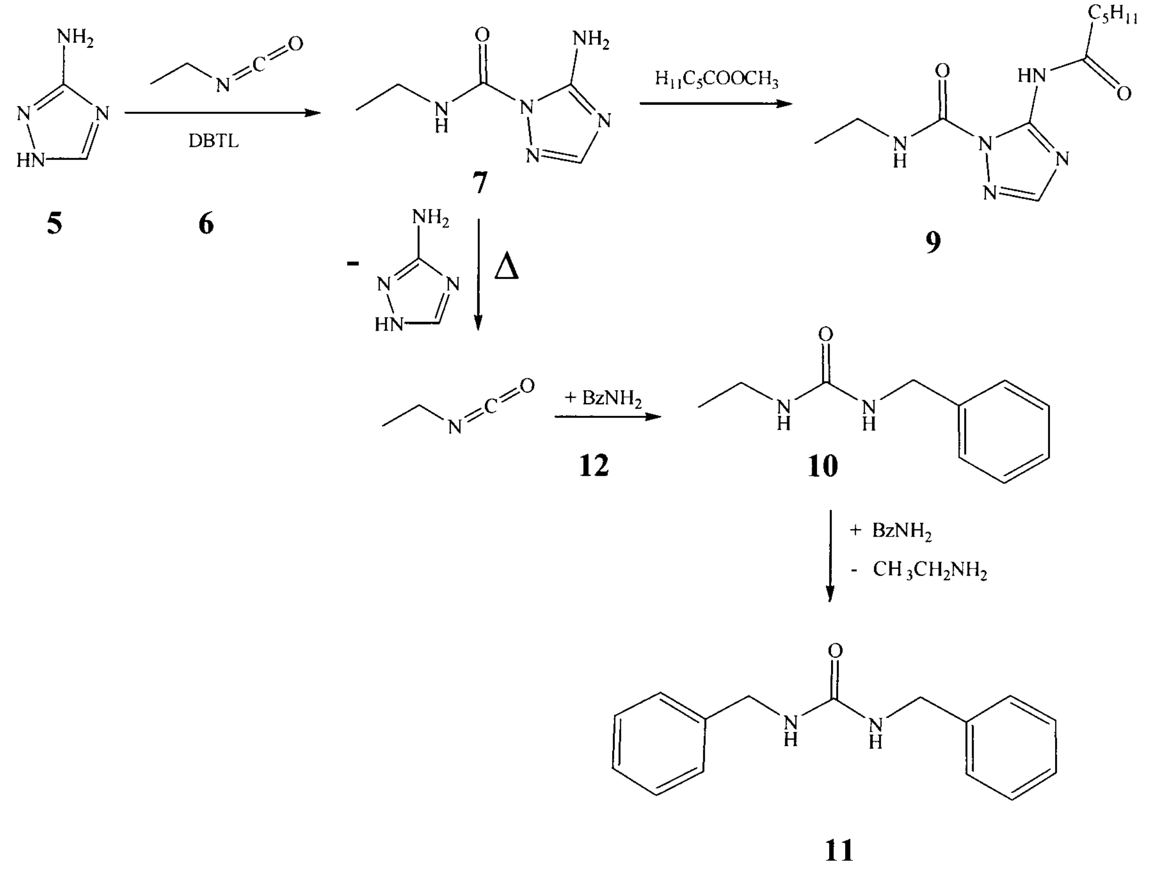


Figure 4. Complex viscosity $|\eta^*|$ [Pa·s] vs temperature [°C] (70–140 °C) of **1** (50 wt % in *N*-methyl pyrrolidone; oscillating measurement, 10 K·min^{-1}, frequency, 1 s^{-1}).

Scheme 2. Postulated Mechanism of Cross-Linking of Copolymer 1



Scheme 3. Synthesis and Subsequent Reactions of (*N*-Methacrylethyl-*N*′-triazoyl)urea (7) (Bz: Benzyl)



Due to the fact that the copolymer **1** contains poorly reactive primary amino groups and methyl ester groups from methyl methacrylate units there is a certain probability for cross-linking reaction yielding amides. In fact, the model molecule **7** and caproic acid methyl ester (**8**) leads to *N*-(3-amidohexyl-(1,2,4-triazol-2-yl)-

N′-ethyl)urea (**9**) but only at very high temperatures above 135 °C and only in very low yields. This indicates that this amide formation may not be the preferred reaction leading to cross-linked structures.

From the results described above, it can be concluded that the new monomer (*N*-methacrylethyl-*N′*-triazoyl)-urea (**2**) can be polymerized to obtain cross-linkable copolymers showing certain unusual rheological behavior in N-MP solution. This monomer may be practically used as a comonomer for development of special coatings or adhesives. In addition, we have found a new protective group for isocyanates that starts the back-formation at relative low temperature in the region of about 130 °C.

Experimental Part

Materials and Methods. Ethyl isocyanate (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany, purity > 97.0%), 2-isocyanatoethyl methacrylate (Sigma-Aldrich Chemie GmbH, purity ≥ 95.0%) and methyl methacrylate (Fluka Chemie AG, Buchs, Switzerland, purity ≥ 99.0%) were obtained and were distilled under reduced pressure. Azoisobutyronitrile (purity ≥ 98.0%), 3-amino-1,2,4-triazole (purity ≥ 97.0%), benzylamine (purity ≥ 99.5%), and caproic acid methyl ester (purity ≥ 99.5%) were also obtained from Fluka. Chloroform-d_1 (99.8 at. % deuterium) and dimethyl-d_6 sulfoxide (99.8 at. % deuterium) were purchased from Deutero GmbH, Kastellaun, FRG. If not mentioned otherwise, all materials were used as received. The ^{1}H NMR spectra (200 MHz) and ^{13}C NMR spectra (50.29 MHz) were recorded on a Bruker AC 200 (room-temperature) in dimethyl-d_6 sulfoxide. For ^{1}H NMR titration a Bruker AM 400 spectrometer and $CDCl_3$ were used. The δ scale relative to TMS was calibrated by the deuterium signal of the solvent as internal standard. The FT-IR spectra were recorded on a Nicolet FT-IR-5 SXB.

GPC measurements were performed with an setup of the company PSS with DMF (0.5 wt % LiBr) as eluent at 75 °C. Calibration was done with polystyrene-standards (PSS) with a range of molecular weight between 374 and 10^6. Applying a flow rate of 1 mL/min, 150 μL of a 0.125 wt % polymer solution in DMF (0.5 wt % LiBr) was put onto a column combination consisting of an HEMA, 10 μm with porosity of 40 Å, as precolumn and 40, 100, and 3000 Å as analytical columns. Detection of the signals was performed with a TSP UV2000 UV−vis detector (254 nm) and a modified Knauer RI detector with toluene as internal standard. The evaluation was performed using PSS-WinGPC 6.1 software.

Melting points (mp) were recorded with a Mettler Toledo FP62 of Mettler Toledo GmbH and are not corrected. The DSC measurements were performed with a DSC-7 of Perkin-Elmer. The heating rate was at 10 and 30 °C·min^{-1}, respectively. The calibration was done with lead and indium as standards. The elemental analyses were performed with a Foss Heraeus vario EL and the mass spectra (FD) with a Finnigan MAT 95 (emitter heating rate: 10 mA/min).

The X-ray structure analysis was prepared on a Diffractometer CAD4 (Enraf-Nonius): radiation, Cu Kα. Tables of crystal data, structure refinement data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for (methacryl-2-ethyl)-*N′*-(3-amino(1,2,4-triazole-2-yl))urea (**2**) may be ordered from the Cambridge Crystallographic Data Centre (CCDC) (www.ccdc.cam.ac.uk) referring to the deposit number CCDC 153136.

Rheological oscillating measurements were performed in the Central Physical Lab of DuPont Performance Coatings, Wuppertal, Germany, with a Bohlin Rheometer VOR system (cone/plate; oscillating frequency, 1 s^{-1}; strain, 0.1−0.2; heating rate, 5 or 10 K·min^{-1}).

Synthesis of (Methacryl-2-ethyl)-*N′*-(3-amino(1,2,4-triazole-2-yl))urea (2). First, 0.84 g (10 mmol) of 3-amino-1,2,4-triazole (**5**) and 0.05 g of DBTL were dissolved in 40 mL of DMF, and then 0.1 g of 4-methoxyphenol was added to inhibit radical polymerization. Under stirring in nitrogen atmosphere at 40 °C, 1.55 g (10 mmol) of 2-isocyanatoethyl methacrylate (**4**) was added dropwise. After 16 h at 50−55 °C, DMF was evaporated partially and the mixture was precipitated in water. The crude product was washed three times with 30 mL of water and dried in a vacuum (1.64 g (69%) of a colorless product; mp 129 °C). ^{1}H NMR (200 MHz), DMSO-d_6, δ/ppm: 8.37 (t, 1H, $^3J_{\mathrm{NHCH_2}}$ = 5.9 Hz, $\mathrm{CH_2N}H$); 7.54 (s, 1H, $\mathrm{N{=}C}H$−triazolyl); 7.20 (s, 2H, $\mathrm{N}H_2$); 6.02 (s, 1H, $\mathrm{C}H_{\mathrm{cis}}\mathrm{H_{trans}{=}CC(O)}$); 5.65 (s, 1H, $\mathrm{CH_{cis}}H_{\mathrm{trans}}\mathrm{{=}CC(O)}$); 4.20 (t, 2H, $^3J_{\mathrm{CH_2CH_2}}$ = 5.4 Hz, $\mathrm{OC}H_2$); 3.46 (m, 2H, $\mathrm{C}H_2\mathrm{NH}$); 1.84 (s, 3H, $\mathrm{C}H_3$). ^{1}H NMR (400 MHz), $CDCl_3$, δ/ppm: 7.43 (s, 1H, $\mathrm{N{=}C}H$−triazolyl); 7.11 (t (br), 1H, $\mathrm{CH_2N}H$); 6.28 (s (br), 2H, $\mathrm{N}H_2$); 6.12 (s, 1H, $\mathrm{C}H_{\mathrm{cis}}\mathrm{H_{trans}{=}CC(O)}$); 5.60 (s, 1H, $\mathrm{CH_{cis}}H_{\mathrm{trans}}\mathrm{{=}CC(O)}$); 4.31 (t, 2H, $^3J_{\mathrm{CH_2CH_2}}$ = 5.3 Hz, $\mathrm{OC}H_2$); 3.67 (dd, 2H, $^3J_{\mathrm{CH_2CH_2}}$ = 5.3 Hz, $^3J_{\mathrm{NHCH_2CH_2}}$ = 5.9 Hz $\mathrm{C}H_2\mathrm{NH}$); 1.93 (s, 3H, $\mathrm{C}H_3$). ^{13}C NMR (50.3 MHz), DMSO-d_6, δ/ppm: 166.42 ($\mathrm{CH_2{=}C(CH_3)}C\mathrm{(O)}$); 156.51 ($\mathrm{NH}C\mathrm{(O)}$); 151.16 ($C\mathrm{H}$−triazolyl); 149.74 ($\mathrm{H_2N}$−$C$); 135.70 ($\mathrm{CH_2{=}}C\mathrm{C(O)}$); 125.79 ($C\mathrm{H_2{=}CC(O)}$); 62.75 ($\mathrm{O}C\mathrm{H_2}$); 38.44 ($C\mathrm{H_2}$-NH); 17.84 ($C\mathrm{H_3}$). FT-IR (KBr), $\tilde{\nu}$/ cm^{-1}: 3430, 3380, 3290, 3230 (ν, NH, br); 2960, 2930 (ν, CH_3, CH_2, CH, m); 1720 (ν, C═O ester (α,β-unsatuared), vs); 1630 (ν, C═O, amide I (urea), s); 1540 (δ, NH, amide II (urea), s); further signals at 1405, 1320, 1300, 1170, 1040, 955. MS (FD): m/z = 239.4 [M$^+$]. Anal. Calcd for $C_9H_{13}N_5O_3$: C, 45.18; H, 5.48; N, 29.27. Found: C, 45.22; H, 5.45; N 29.26.

Copolymerization of (Methacryl-2-ethyl)-*N′*-(3-amino-(1,2,4-triazole-2-yl))urea (2) and Methyl Methacrylate (3). A monomer mixture of 1.0 g (4.18 mmol) of **2** and 2.09 g (20.91 mmol) of **3** were dissolved in 30 mL of DMF, and 0.33 g (2.01 mmol) of AIBN (8 mol %) was added. The solution was heated to 80 °C while stirring under nitrogen atmosphere. After 12 h, the polymerization reaction was stopped by cooling and the solution was poured into 250 mL of water yielding colorless polymeric products. The resulting crude polymer was dissolved in 10 mL of THF, poured into 100 mL of water yielding colorless, solid polymeric product after drying (86% of a colorless polymer). ^{1}H NMR ($CDCl_3$), δ/ppm: 7.10−6.90 (m (br), (H-triazolyl); 4.13 (s (br), $\mathrm{OC}H_2\mathrm{CH_2NHC(O)}$); 4.40−3.10 (s, $\mathrm{OC}H_3$); 2.30−1.25 (m, $\mathrm{C}H_2$); 1.20 (s, $\mathrm{C}H_3$-it); 1.00 (s, $\mathrm{C}H_3$-at); 0.80 (s, $\mathrm{C}H_3$-st). FT-IR (KBr), $\tilde{\nu}$/ cm^{-1}: 3430 (ν, NH, vbr); 2995, 2950 (ν, CH_3, CH_2, CH, m); 1730 (ν, C═O−ester, vs); 1670 (ν, C═O, amide I (urea), s); 1555 (δ, NH, amide II (urea), m); further signals, 1440, 1270, 1240, 1195, 1155, 990. DSC (heating rate: 10 °C·min^{-1}): onset = 117 °C; end = 138 °C; $Cp_{1/2}$ = 126 °C. GPC: $\bar{M}_{\mathrm{n}}$ = 1300, $\bar{M}_{\mathrm{w}}$= 3.780, D = 2.9.

Synthesis of *N*-(3-Amino(1,2,4-triazol-2-yl)-*N′*-ethyl)-urea (7). First, 3.2 g (38.1 mmol) of 3-amino-1,2,4-triazole (**5**) and 0.1 g of DBTL were suspended in 100 mL of acetone. With stirring under nitrogen atmosphere, 2.84 g (40.0 mmol) ethyl isocyanate (**6**) dissolved in 50 mL of acetone was added slowly, and the turbidic mixture changed into a clear solution. After this mixture was stirred for 6 h at 50 °C, the solvent was removed and the crude product was washed three times with 25 mL of hexane (5.4 g (91%) of a colorless product; mp 91 °C). ^{1}H NMR (DMSO-d_6), δ/ppm: 8.23 (t, 1H, $^3J_{\mathrm{NHCH_2}}$ = 5.9 Hz, $\mathrm{N}H\mathrm{CH_2}$); 7.52 (s, 1H, $\mathrm{C}H$); 7.20 (s (br), 2H, $\mathrm{N}H_2$); 3.21 (m, 2H, $\mathrm{C}H_2$); 1.04 (t, 3H, $^3J_{\mathrm{CH_3CH_2}}$ = 7.3 Hz, $\mathrm{C}H_3$). ^{13}C NMR (DMSO-d_6), δ/ppm: 156.46 ($C\mathrm{(O)}$); 150.76 ($C\mathrm{NH_2}$); 149.53 (C═N−triazolyl); 34.26 ($C\mathrm{H_2}$); 14.67 ($C\mathrm{H_3}$). MS (FD): m/z = 155,6 [M$^+$]. Anal. Calcd for $C_5H_9N_5O$: C, 38.70; H, 5.85; N, 45.14. Found: C, 39.17; H, 5.81; N, 44.26.

Synthesis of *N*-(3-Amidohexyl-(1,2,4-triazol-2-yl)-*N′*-ethyl)urea (9). First, 1.0 g (6.44 mmol) of **7**, 0.2 g of ammonium chloride and 5 mL of methyl caproate (**8**) were stirred under nitrogen atmosphere for 10 h at 135 °C. The residual methyl caproate was removed, and the crude product was dissolved in methanol. After filtration the solvent was removed and the product was dried in a vacuum (0.8 g (49%) of a slightly yellow powder (mp 64 °C). ^{1}H NMR (DMSO-d_6), δ/ppm: 13.33 (s, 1H, $\mathrm{N}H\mathrm{C(O)CH_2CH_2}$); 8.24 (t, 1H, $^3J_{\mathrm{NHCH_2}}$ = 5.9 Hz, $\mathrm{N}H\mathrm{CH_2}$); 7.67 (s, 1H, $\mathrm{C}H$); 2.97 (m, 2H, $\mathrm{NHC}H_2$); 2.36 (t, 2H, $^3J_{\mathrm{CH2CH_2}}$ = 7.3 Hz, $\mathrm{NHC(O)C}H_2\mathrm{CH_2}$); 1.57 (m, 2H, NHC-(O)$\mathrm{CH_2C}H_2$); 1.28−1.00 (m, 7H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$, $\mathrm{NHCH_2C}H_3$); 0.86 (t, 3H, $^3J_{\mathrm{CH_3CH_2}}$ = 6.4 Hz, $\mathrm{CH_2CH_2C}H_3$). MS (FD) (253.3): m/z = 253.5 [M$^+$].

Synthesis of (*N*-Benzyl-*N*′-ethyl)urea (10) and dibenzylurea (11). First, 0.4 g (2.58 mmol) of **7** was dissolved in 3.0 g (28 mmol) of benzylamine (**12**). The suspension was stirred under nitrogen atmosphere for 10 min at 120 °C. The residual benzylamine was removed and the product was dried in a vacuum. MS (FD): $m/z = 84.5$ (4) [aminotriazole], 178.7 (11) [**10**], 240.8 (100) [**11**].

Back-Formation of Ethyl Isocyanate (6) from *N*-(3-Amino(1,2,4-triazol-2-yl)-*N*′-ethyl)urea (7). First, 0.5 g (3.2 mmol) of *N*-(3-amino(1,2,4-triazol-2-yl)-*N*′-ethyl)urea (**7**) was heated under nitrogen atmosphere for 15 min at 140 °C. The resulting fluid was collected on a KBr pellet. FT-IR (KBr), $\tilde{\nu}$/cm^{-1}: 2990, 2940 (ν, CH, m); 2280 (ν, NCO, vs); further signals at 3435, 3100, 1690, 1360, 1350.

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