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Reaction behaviour of monomeric β-ketoesters

3. Polymerizable reaction products of 2-acetoacetoxyethyl methacrylate with aromatic isocyanates and aldehydes

Norbert Moszner, Frank Zeuner, Ulrich Salz, and Volker Rheinberger

Ivoclar AG, Bendererstrasse 2, FL-9494 Schaan, Liechtenstein

Summary

The addition of 2-acetoacetoxyethyl methacrylate (AAEMA) to aromatic isocyanate such as phenyl isocyanate or tolylene 2,4-diisocyanate, and the Knoevenagel condensation of AAEMA with aromatic aldehydes, respectively, yield polymerizable products. These monomers were characterized by elemental analyses, IR, ^{1}H NMR and partially by ^{13}C NMR spectroscopy. The radical polymerization of synthesized AAEMA-isocyanates adducts forms polymeric blocked isocyanates. The Knoevenagel condensate of AAEMA with benzaldehyde is radically polymerizable and tends to crosslink during its homopolymerization.

Introduction

β–Ketoesters such as acetoacetates are easy available from corresponding hydroxyl group containing compounds by the reaction with diketene [1] or by transesterification with t-butyl acetoacetates [2]. β–Ketoesters shows various possibilities to react with organic compounds like amines, aldehydes, acrylates or metal salts at ambient temperature with pronounced rate [3]. Thus acetoacetates react with aliphatic aldehydes [4] or benzaldehyde [5] in the presence of catalytic piperidine at -5-0 °C yielding alkylidene or benzyliden acetoacetates via Knoevenagel condensation. The reaction with aldehydes or the enamine formation as a method of crosslinking of acetoacetylated polymers with dialdehydes or diamines has been reported [6,7]. The use of these reactions to crosslink acetoacetylated resins appear to be an attractive alternative to the use of isocyanate crosslinking reagents, because it provides ambient-temperature curing and can be used in both water- and solvent-borne applications.

Previously, we reported about the synthesis, characterization and polymerization of various enamines formed by the reaction of AAEMA with aliphatic mono- and diamines and about the metal chelation with AAEMA [8].

In this paper the reaction of AAEMA with aromatic isocyanates and aldehydes, and characterization and polymerization of the monomeric reaction products are presented.

Experimental

Materials

AAEMA (Lonza) was used with purity of about 96% and contained 2-hydroxyethyl methacrylate (about 3.0%) and methacrylic acid (about 0.5%). Phenyl isocyanate (PI), tolylene 2,4-diisocyanat (TDI), aromatic aldehydes (Fluka), 2-hydroxyethyl methacrylate (HEMA, Röhm) and stannous dioctylcarboxylate (Metatin 801, Acima) were used without further purification.

Dimethylformamide (DMF), and 2,2-azobisisobutyronitrile (AIBN) were purified as described previously [9]. 2,6-di-tert.-butyl-4-methylphenole (BHT), anhydrous tetrahydrofuran (THF, Fluka) and diethyl ether (Fluka) were used in analytical grade without further purification.

Synthesis

Addition of AAEMA to PI:

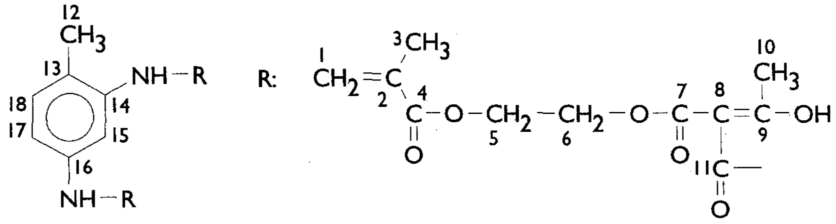
In a typical isocyanate reaction, to a mixture of 60 mmol AAEMA, 350 mg Metatin 801 (catalyst) and 50 mg BHT (inhibitor) 60 mmol PI was added under stirring at room temperature. After 48 h the formed yellow crystalline product was recrystallized from a diethyl ether/petroleum ether mixture obtaining the AAEMA-PI adduct (**1**, 3-oxa-4,6-dione-5-(N-phenyl)carbamoyl-heptyl methacrylate) as white crystalls (m.p.: 50 °C) in 88 % yield.

$C_{17}H_{19}NO_6$ (333.3 g/mol): found: C: 61.30 (calculated: 61.26), H: 5.66 (5.75), N: 4.25 (4.20). ^1H NMR ($CDCl_3$, δ (ppm)): 1.96 (s,3H,$=C(CH_3)$-), 2.48 (s,3H,$=C(OH)$-$C\underline{H}_3$), 4.44-4.52 (m,4H,-CH_2-CH_2-), 5.61 and 6.14 (s,2H, $=CH_2$), 7.13-7.53 (m,5H,Ar-H), 11.17 (s,1H,-NH-) and 18.33 (s,1H,$=C(O\underline{H})$-CH_3). ^{13}C NMR ($CDCl_3$, δ (ppm), assigment of carbon atoms compare scheme 1): 18.3 (C3), 26.5 (C10), 62.3 and 62.6 (C5,C6), 94.6 (C8), 121.8 (C13), 125.0 (C15), 126.2 (C1), 129.0 (C8), 135.9 (C2), 136.8 (C12), 167.0 (C4), 168.8 (C11), 170.8 (C7) and 192.9 (C9). IR (film, cm^{-1}): 3430 (OH), 3250 (NH), 1722 and 1673 (C=O), 1638 (C=C).

Addition of AAEMA to TDI:

The addition of AAEMA to TDI was carried out analogously to the PI addition. After 4 weeks the yellow solid crude product was recrystallized from ethanol obtaining the AAEMA-TDI adduct (**2**) as light yellow crystalls (m.p.: 105 °C) in 24 % yield.

$C_{29}H_{34}N_2O_{12}$ (602.6 g/mol): C: 57.97 (57.80), H: 5.76 (5.69), N: 5.27 (4.65). ^1H NMR ($CDCl_3$, δ (ppm)): 1.95 (s,6H,$=C(CH_3)$-), 2.29 (s,3H, Ar-CH_3), 2.48 (s,6H,$=C(OH)$-$C\underline{H}_3$), 4.30 (s,8H,-CH_2-CH_2-), 5.61 and 6.13 (s,4H, $=CH_2$), 7.15-8.08 (m,5H,Ar-H), 11.05-11.26 (m,2H,-NH-) and 15.72 (s,2H,$=C(O\underline{H})$-CH_3). ^{13}C NMR ($CDCl_3$, δ (ppm)): 17.7 (C12), 18.3 (C3), 26.5 (C10), 62.3 and 62.6 (C5,C6), 94.6 (C8), 116.2 and 118.5 (C15,C17), 126.3 and 126.4 (C1, C13), 130.7 (C18), 135.2, 135.6 and 135.8 (C2,C14,C16), 167.0 (C4), 168.8 (C11), 170.7 (C7) and 193.0 (C9). IR (film, cm^{-1}): 3422 (OH), 3241 (NH), 1721 and 1675 (C=O), 1632 (C=C).



Addition of HEMA to PI

N-Phenyl methacrylatoethyl carbamate (**3**) was prepared by the reaction of PI with HEMA with Metatin 812 as catalyst analogous to the procedure reported in [10] obtaining a wax like substance (m.p. 46 °C, 43 °C [10]) in 94 % yield.
^{1}H NMR ($CDCl_3$, δ (ppm)): 1.97 (s,3H,=$C(CH_3)$-), 4.40 (s,4H,-CH_2-CH_2-), 5.58 and 6.17 (s,2H, CH_2=), 6.78 (s,1H,-NH-) and 7.00-7.48 (m,5H,Ar-H). IR (film, cm^{-1}): 3340 (NH), 1730 and 1720 (C=O), 1630 (C=C).

Knoevenagel condensation of AAEMA and benzaldehyde

A mixture of 100 mmol AAEMA and 100 mmol benzaldehyde in 30 ml THF was cooled to -5 °C. Piperidine (0.2 g) in 1 ml ethanol was added slowly, so that the heat of reaction did not cause the temperature to rise above 5 °C. Then the mixture was cooled to 0°C and stored overnight. After 24 h standing at room temperature the solvent was evaporated in weak vacuo. The residue was disolved in 100 ml ether and washed with acetic acid (1%), NaOH (1N), saturated NaCl solution and water. The organic phase was dried over anhydrous $NaSO_4$ and the solvent was evaporated in vacuo yielding 2-methacryloyloxyethyl 3-(benzylidene)-acetoacetate (**4**) as a yellow viscous liquid in 67 % yield. Attempted purification of the crude product by distillation in high vacuum failed was notsuccesful.

^{1}H NMR ($CDCl_3$, δ (ppm)): 1.87 and 1.93 (s,3H,=$C(CH_3)$-), 2.33 and 2.42 (s,3H, -CO-CH_3), 4.32-4.62 (m,4H,-CH_2-CH_2-), 5.48, 5.58, 6.00 and 6.17 (s,2H, CH_2=) and 7.35-8.02 (m,6H,Ar-H and =CH-Ar). IR (film, cm^{-1}): 1721 and 1665 (C=O), 1624 (C=C).

2-Methacryloyloxyethyl 3-(4-bromobenzylidene)-acetoacetate (**5**) was prepared analogously to **4** and was obtained as a yellow viscous liquid in 64 % yield.

^{1}H NMR ($CDCl_3$, δ (ppm)): 1.88 and 1.95 (s,3H,=$C(CH_3)$-), 2.33 and 2.42 (s,3H, -CO-CH_3), 4.33-4.65 (m,4H,-CH_2-CH_2-), 5.57-5.67 (m) and 6.05 and 6.15 (s,2H, CH_2=) and 7.25-7,83 (m,6H,Ar-H and =CH-Ar). IR (film, cm^{-1}): 1722 and 1666 (C=O), 1624 (C=C).

2-Methacryloyloxyethyl 3-(4-methoxybenzylidene)-acetoacetate (**6**) was prepared analogously to **4** and was obtained as a yellow viscous liquid in 62 % yield.

^{1}H NMR ($CDCl_3$, δ (ppm)): 1.87 and 1.95 (s,3H,=$C(CH_3)$-), 2.33 (s,3H, -CO-CH_3), 3.82 and 3.88 (s,3H,Ar-O-CH_3), 4.22-4.67 (m,4H,-CH_2-CH_2-), 5.55, 5.60, 6.08 and 6.17 (s,2H, CH_2=) and 6.83-8.023 (m,5H,Ar-H and =CH-Ar). IR (film, cm^{-1}): 1720 and 1700 (C=O), 1636 (C=C).

Ethyl 3-(benzylidene)-acetoacetat (**7**) was prepared according to [11]. The formed 64:36 (mol-%) mixture of cis-trans isomers was separated by MPLC using a SiO_2-column and a n-hexane/ethyl acetate mixture 75:25 as eluent giving the pure isomers **7a** and **7b**:

^1H NMR ($CDCl_3$, δ (ppm)): **7a**: 1.33 (t,3H,-CH_3), 2.37 (s,3H, -CO-CH_3), 4.28 (q,2H,-CH_2-), 7.37 (s,5H,Ar-H) and 7.65 (s,1H,=CH-Ar); **7b**: 1.26 (t,3H,-CH_3), 2.42 (s,3H, -CO-CH_3), 4.33 (q,2H,-CH_2-), 7.44 (s,5H,Ar-H) and 7.81 (s,1H,=CH-Ar).

Polymerization

The polymerizations of monomers were carried out in sealed glass tubes. After a given amount of AIBN was dissolved in DMF, the monomer was introduced. The tubes were degassed through three freeze-thaw cycles (liquid nitrogen) before they were placed in a constant-temperature bath (60 °C). After a given time the homopolymerization was terminated by the addition of excess methanol. The monomer conversion was calculated from the gravimetrically determined yields of the dried polymers. The polymer was repricipitated from THF/methanol and dried under vacuo to constant weight.

Poly(**1**) (M_n = 74200 g/mol): ^1H NMR ($CDCl_3$, δ (ppm)): 0.73-1.38 (m,5H, -CH_2-C(CH_3)<), 2.37-2.53 (s,3H,=C(OH)-C$\underline{H}_3$), 3.98-4.58 (m,4H,-CH_2-CH_2-), 7.05-7.60 (m,5H,Ar-H) and XX.XX (s,1H,=C(O$\underline{H}$)-CH_3).

Poly(**4**) (M_n = 67000 g/mol): ^1H NMR ($CDCl_3$, δ (ppm)): 0.57-2.08 (m,5H, -CH_2-C(CH_3)<). 2.30 and 2.37 (s,3H,-CO-CH3), 3.87-4.70 (m,4H,-CH_2-CH_2-), 7.40 (m,5H,Ar-H), 7.60 and 7.71 (s,1H,=CH-Ar).

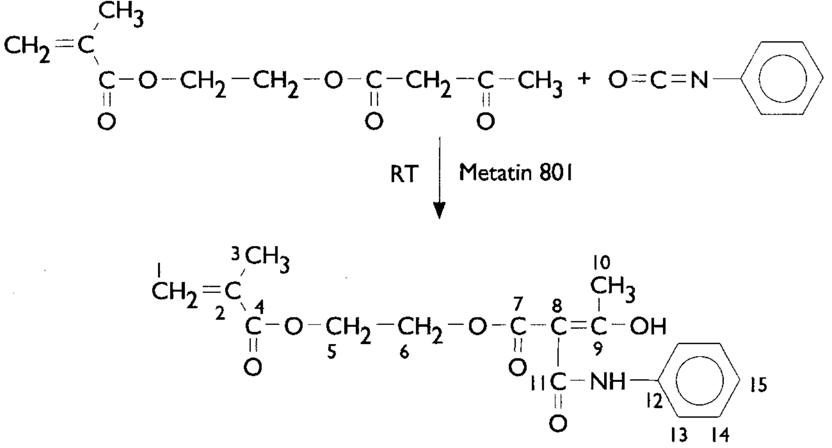
Measurements

^1H NMR measurements were recorded on an EM 390 (Perkin-Elmer, 90 MHz) using tetramethylsilane (TMS) as the standard. ^{13}C NMR spectroscopic measurements were performed with a AC 300F spectrometer (Bruker, 300 MHz) using $CDCl_3$ or dimethylsulfoxide-d_6 as a solvent. An FT-IR spectrometer 1600 (Perkin-Elmer) was used to record IR spectra. The number-average molecular weights of polymers were determined by GPC using a isocratic pump IsoChrom (Spectra-Physics) and THF as eluent, an detector RI-4 (Varian) and colums calibrated with poly(MMA) standards. MPLC investigations were carried out using a MPLC pump Büchi 681, fraction collector Büchi 684, an MPLC column 28239 (Büchi AG) and a RI detector Präparativ (Knauer). The stationary phase was Kieselgel 40 (Fluka) and as eluent a mixture of hexane/ethyl acetate was used. Differential scanning calorimetry (DSC) measurements were performed by using a Perkin-Elmer DSC-7 thermal analyzer. Scanning rates of 10 °C/min were used.

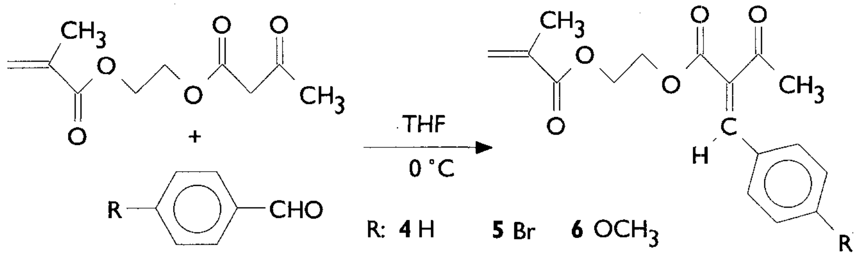
Results and Discusion

The monomers **1** and **2** were obtained by the addition of AAEMA to PI (scheme 1) or TDI as crystalline compounds. The reaction of AAEMA with aliphatic isocyanates such as for example 2,2,4-trimethyldiisocyanate failed. The addition to this isocyanate is to slow and was accompanied by polymerization of the formed adduct. Characterization of AAEMA-isocyanate adducts was carried out by ^1H NMR, ^{13}C NMR and IR spectroscopy and elemental analysis, respectively. The ^1H NMR spectra of compounds **1** and **2** show the expected signals of protons of methacrylate or $-CH_2-CH_2-$ group analogous to AAEMA at 5.6 (1H,s) and 6.1 (1H,s) or 4.3-4.5 ppm (4H,m). The protons of both methyl groups of AAEMA give two singlets at 1.95 (3H, $=C(CH_3)-$) and 2.27 ppm (3H, $-CO-CH_3$). In contrast, the signals of the aceto group methyl protons are displaced down field to 2.48 ppm corresponding to the expected signal of methyl protons of enol form. The formation of **1** and **2** in the enol form is also confirmed by appearance the enolprotons at 18.3 and 15.6 ppm, and the chemical shift of carbon atoms of the $=C(OH)-$ group at 192.9 and 193.0 ppm. For assigment of the observed ^{13}C NMR signals chemical shift increments compiled by Pretsch et al. [12] and the DEPT (distortionless enhancement by polarization transfer) experiment [13] were used.

Scheme I



The Knoevenagel condensation of benzaldehydes with AAEMA in an equimolar ratio was carried out using piperidine as catalyst at 0°C, which were found to be the best conditions for the preparation of unsaturated products [14]:



The ^1H NMR spectra of condensates **4-6** show 2 singlets for the signals of methylprotons in the $=C(CH_3)-$ and $-CO-CH_3$ group, respectively. Further, also the expected singlets for the protons of the methacrylate double bond are splitt. This can be due to formation of mixture of E-/Z-isomers of **4-6** by Knoevenagel condensation. This is confirmed by the fact, that the ^1H NMR spectra of the isomers of ethyl benzylidene acetoacetate **7a** and **7b**, which were separated by MPLC; show only the expected singlets.

Table 1 Polymerization of monomers **1-3** in the presence of AIBN (0.02 mol/l) in THF at 60 °C

Monomer	[Monomer]	Time (min.)	Conversion (%)	M_n (g/mol)	T_G (°C)
1	1.00	20	30.0	-	-
1	1.00	60	62.7	74200	-
1	1.00	120	86.4	-	-
1	0.50	60	34.2	30700	70
1	0.75	60	41.4	49200	-
1	1.25	60	60.7	97500	72
2[a]	0.50	20	59.0[b]	-	-
2[a]	0.50	60	91.9	-	-
3	1.00	60	66.6	95700	-
3	0.50	60	82.6	55700	-
3	0.75	60	93.5	82600	-
3	1.50	60	64.2	138000	89

[a] DMF as solvent. [b] Gelation time: 11 Minutes.

Table 2 Polymerization of monomers **4-6** in the presence of AIBN (0.02 mol/l) in DMF at 60 °C

Monomer	[Monomer]	Time (min.)	Conversion (%)	M_n (g/mol)
4	1.00	15	15.5	200000
4	1.00	30	31.8	123000[a]
4	1.00	60	57.8	-
4	0.50	30	26.0	70000
4	0.75	30	32,3	94000
5	1.00	30	41.2	-
6	1.00	30	39,4	-

[a] T_G: 60 °C.

The synthesized monomers were radically polymerized with AIBN as initiator in THF or DMF. In case of monomer **1** homopolymers were obtained with a number-average molecular weight between 30700-97500 g/mol (Tab. 1). The glass transition temperature (T_G) of poly(**1**) of about 70 °C is significantly higher than the T_G of poly(AAEMA) (0-2°C) or of polymeric enamines derived from AAEMA (9 to -42 °C [8]) which is attributed to the polar carbamoyl and bulky phenyl groups in **1**. This confirmed by the fact, that T_G of the polymeric carbamate poly(**3**), which is a polymerized adduct of PI and HEMA, is about 89 °C. As expected the polymerization of the difunctional monomer **2** yielded a crosslinked polymer. In result of the radical polymerization of synthesized AAEMA-isocyanates adducts polymeric blocked isocyanates are formed.

The 2-methacryloyloxyethyl 3-benzylideneacetoacetates **4-6** are easily radically polymerizable. For example, in with **4** polymers with a number-average weight in the range of 70000 to 200000 g/mol were obtained. The molecular monomers **4-6** tend to crosslink. For example, in case of **4** the sample with a polymerization time of 1 hour were crosslinked and poly(**5**) and poly(**6**), respectively. The nature of crosslinking is being further inverstigated.

The Knoevenagel condensates of AAEMA and 1-naphthaldehyde or terephthalaldehyde, respectively, showed high polymerization tendency and were therefore not isolated in a pure form.

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