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Crosslinking of carboxyl functional (meth)acrylate copolymers with bisketeneimine

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Summary

The bisketeneimine $Ph_2C{=}C{=}N{-}C_6H_4{-}N{=}C{=}CPh_2$ **1** has been used as a crosslinker for carboxyl functional (meth)acrylate copolymers of various molar masses, in which the COOH group is attached to the backbone through spacers of various length. The crosslinking reaction, carried out at various temperatures, was monitored by infrared spectroscopy and by dynamic mechanical analysis. From a modelreaction with nonanoic acid kinetic parameters were calculated. The products poly(meth)acrylate-polyimide networks were characterised by NMR and FTIR spectroscopy. The thermal stability (TGA measurement) was comparable to that of a corresponding polyurethane.

Introduction

Multifunctional heterocumulenes like polyisocyanates are extensively used in the coatings industry as crosslinkers for several types of prepolymers including hydroxyl-functional methacrylic and acrylic copolymers (1).

For carboxyl-functional prepolymers polycarbodiimides and polyketeneimines are suitable in principle as crosslinkers. However, carbodiimides react with carboxylic acids to give thermally unstable N-acylurea's (2). Keteneimines on the other hand were expected to give stable N-acylamide crosslinks upon reaction with carboxyl-functional prepolymers. Linear poly(N-acylamides) have been prepared by Kurita et al. (3), who found a good thermal stability of these polymers by thermogravimetric analysis.

Apart from stucture-properties relations of the bisketeneimine generated networks we were also interested in the kinetics of this new type of network formation compared to analogous isocyanate and carbodiimide reactions.

Results and discussion

Modelreaction

Bisketeneimine **1** was first reacted with nonanoic acid **2** to the imide **3**, see Scheme 1, as a model for the crosslinking reaction at 80°C to 130°C, a suitable temperature range for the network formation. The reaction was monitored by measuring the disappearance of the $-N{=}C{=}C<$ absorption at 1993 cm^{-1} (fig.1).

According to this criterion, the reaction is complete at about 160 min at 130°C, whereas at 100°C much longer reaction times were needed. During the reaction two characteristic imide absorptions appeared at 1693 and 1717 cm^{-1}, while the 1736 cm^{-1} C=O absorption of the acid **2** was eliminated gradually.

Kurita et al (3) found absorptions at 1650-1660 cm^{-1} and at 1710-1720 cm^{-1} (shoulder) for the

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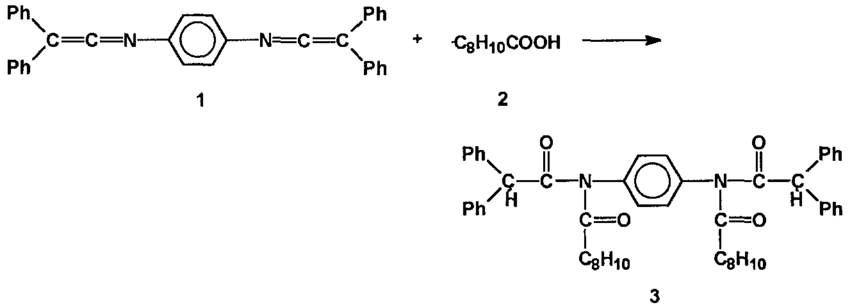


Scheme 1

linear polymer prepared from bisketeneimine **1** and a dicarboxylic acid. They tentatively attributed the former bands to diphenylacetamido end groups arising from hydration of the keteneimine in the process of anhydride formation from the acid. In our case however no anhydride bands (expected at about 1765 and 1830 cm^{-1}) could be detected. With ^{1}H and ^{13}C NMR spectroscopy the reaction and the product **3** could be conclusively characterised. Two typical diphenyl-methine protons appear at 5.48 ppm, well separated from the aromatic and aliphatic proton regions. The four methylene protons of the two -CH$_2$C(O)- moieties appear at 2.68 ppm as a triplet. In the ^{13}C NMR spectrum the absorption of the middle carbon atom of the keteneimine moiety (>C=C=N) in **1** disappears during the reaction, giving way to two carbonyl peaks at 174.5 and 176.2 ppm (-CH$_2$C(O)- and >CHC=O respectively). More details of these spectra are given in the experimental part.

Kinetic parameters were calculated from the temperature dependence of the first order disappearance of bisketeneimine in the model reaction: $\Delta H^{\ddagger} = 68$ kJ/mol and $\Delta S^{\ddagger} = -87$ J/K·mol. Similar values were found for the carbodiimide-COOH reaction (4) e.g. N-acylurea formation from diphenylcarbodiimide and 5-phenylpentanoic acid: $\Delta H^{\ddagger} = 68$ kJ/mol

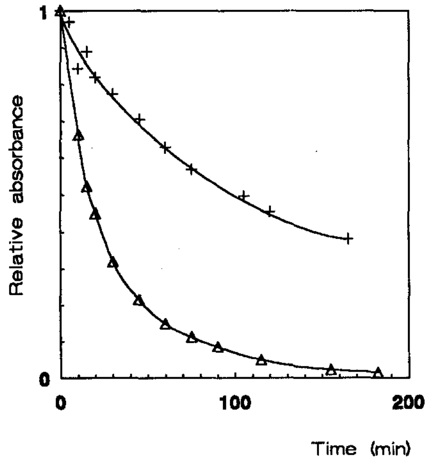


Fig. 1. Course of the reaction of n-nonanoic acid **2** with bisketeneimine **1** at + 100°C and Δ 130°C.

TABLE 1.

Polymer	MMA%1)	BuA%1)	MCOOH%1)	$\bar{M}_n$ 2)	$\bar{M}_w$ 2)	Tg °C3)
P4	58.0	34.0	8.0	13000	33000	36
P5	57.8	30.8	11.4	16000	41000	43
P6	55.6	31.2	13.2	9800	24000	25

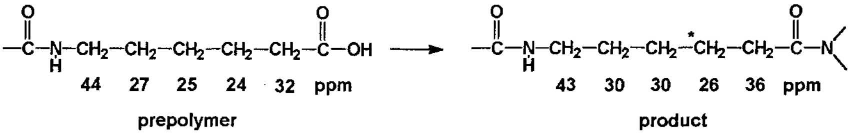
1) mol%, ^{13}C NMR data; 2) GPC data, polystyrene standards; 3) DSC data.

and $\Delta S^\ddagger$ = -79 J/K·mol. The negative $\Delta S^\ddagger$ is consistent with steric ordering in the transition state, characteristic of addition reactions on such cumulene systems. Unfortunately kinetic data from the literature on the isocyanate/OH reaction show considerable scattering, making a sound comparison with the keteneimine reaction difficult.

Crosslinking experiments

The carboxyl functional methacrylic monomers used in this study were methacrylic acid **4**, 6-(methacrylamido)hexanoic acid **5** and 11-(methacrylamido)undecanoic acid **6**, the latter two synthesized from methylmethacrylate and the corresponding amino acid. These were copolymerized with butylacrylate and methylmethacrylate with suitable radical initiators. The copolymer composition (see table 1) was determined by ^{13}C NMR, from the -C(O)O-*CH$_2$- (indicated) signals at 64.2 ppm in n-butylacrylate and at 51.6 ppm in methylmethacrylate and the -C(O)NH-*CH$_2$- (indicated) signal at 44.4 ppm in monomer **5** and **6**. The quantitative ^{13}C NMR analysis is justified in this case, where the nuclear Overhauser effect was found to be equal for the investigated resonances, in concentrated (25-30% w/v) solutions (5).

The crosslinking reactions of the prepolymers (**P4**, **P5**, **P6**) with bisketeneimine **1** were carried out by heating films casted from THF solutions at various temperatures. The resulting polyimide networks were characterised by ^{13}C MAS and CP-MAS NMR spectroscopy using data from the model reaction described above. When comparing the spectra from e.g. the prepolymer **5** and the network prepared from **5** and bisketeneimine **1**, the following significant features emerge (see fig. 2): aromatic absorptions at 128.5 and 139 ppm and the diphenylmethine carbon signal just visible as a shoulder at 68.2 ppm are introduced into the product by the crosslinking reaction. Further a peak sharpening at 26 ppm is due to the indicated methylene carbon atom in the spacer group (Scheme 2) in the crosslinked product, having a chemical shift, markedly different from its neighbours. In the prepolymer spacer group the three middle carbon atoms have only slightly different chemical shifts giving rise to a broad absorption between 24 and 27 ppm. This assignment correlates well with literature data on polyamides (6).



Scheme 2. ^{13}C CP-MAS NMR chemical shifts of the spacers in the prepolymer and in the crosslinked product.

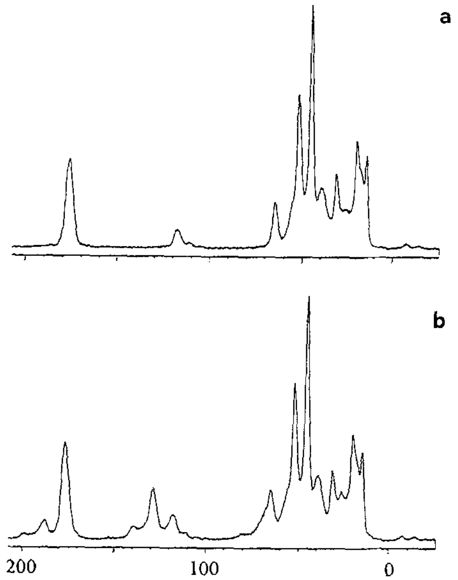


Fig. 2. ^{13}C CP-MAS NMR spectra of a. Prepolymer **P5**, and b. The network from **P5** and bisketeneimine **1**

FTIR data are also consistent with the structure: the keteneimine absorption at 1993 cm^{-1} has disappeared, and one C=O imide absorption is just visible (about 1710 cm^{-1}) as a shoulder on the C=O ester peak at 1733 cm^{-1}. The kinetics of the keteneimine crosslinking were compared with those of a polyurethane system based on an hydroxyl functional acrylic copolymer of similar composition and MDI (4,4'-diphenylmethanediisocyanate). These reactions were monitored again by FTIR, observing disappearances of the keteneimine and isocyanate absorptions at 1993 and 2230 cm^{-1} respectively (see fig. 3). The results indicate that the isocyanate crosslinking is faster than the ketenimine crosslinking over the whole temperature range investigated. The keteneimine crosslinking of the three prepolymers **P4**, **P5** and **P6** showed similar rates, no significant influence of the spacer length was observed.

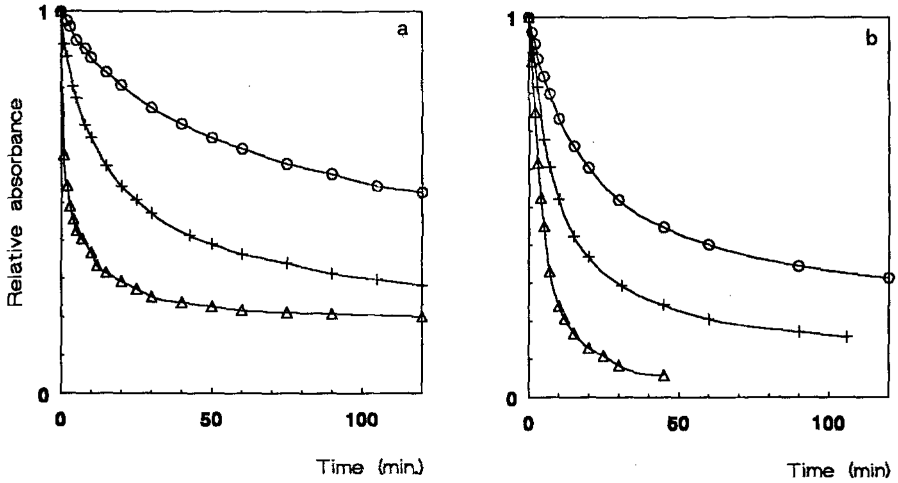


Fig. 3. Crosslinking rates of a. **P5** with bisketeneimine **1**, and b. an OH-functional acrylic copolymer (MMA 57.9%; BuA 32.0%; hydroxyethylmethacrylate 10.1%; $\bar{M}n$= 19,400, $\bar{M}w$= 55,000, Tg = 58°C) with MDI at O 80°C; + 100°C and Δ 130°C.

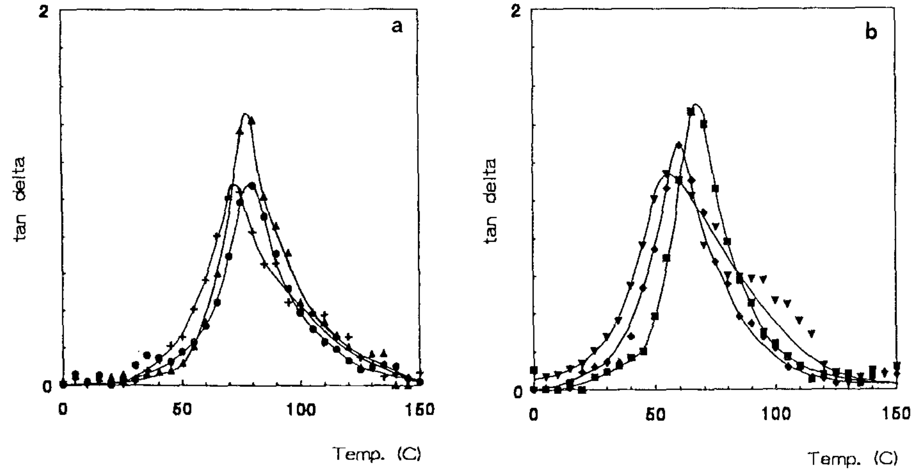


Fig. 4. Dynamic spring analysis for samples crosslinked with bisketeneimine for various times at 100°C. a. P5: + 30 min, ▲ 60 min, • 120 min and b. P6: ▼ 15 min, ♦ 30 min, ■ 60 min.

The crosslinking reaction has also been followed by dynamic spring analysis (7), (see experimental part) monitoring tg δ (E"/E', loss modulus over storage modulus) as a function of temperature for various crosslinking times. From fig. 4 it is clear that the maximum in tg δ, corresponding to the Tg of the network, shifts to higher temperatures with increasing crosslink density, remaining constant when crosslinking is complete. For **P5** this shift is from 43°C to 81°C and for **P6**, which has a lower Tg due to the longer spacer, from 25°C to 69°C. The acrylic acid based systems (P4, COOH directly connected to the backbone, spacer n=0) could not be analyzed in this way because of brittleness. Log E' against temperature for the samples cured at 100°C for 30, 60 and 120 min also reveal the Tg shifts.

Thermogravimetric analyses under nitrogen as well as in air have been carried out for both polyurethane acrylic and polyimide acrylic networks. The results indicate that according to this method thermal stability of the bisketeneimine network is comparable to that of the polyurethane systems. In air 10% weight loss occurs at about 330 °C, and 90% weight loss at 500°C. The prepolymers show similar behaviour. The linear polymers from diacids and bisketeneimine **1**, described by Kurita (3), showed 10% weight loss at about 275°C but retained 30% to 60% weight at 500°C. Apparently, the thermal stability of the network is more dependent on the prepolymers. No significant improvement of stability was observed when the TGA measurements were carried out under nitrogen.

Experimental

Bisketeneimine **1** was a gift of AKZO, Arnhem, The Netherlands. All vinyl monomers were commercial samples, destillated immediately prior to use. NMR spectra were recorded on a Varian VXR-400S spectrometer, ^{13}C CP-MAS and MAS NMR spectra were recorded on a Bruker AM 400 spectrometer. DSC measurements were carried out on a Perkin Elmer DSC-7, TGA measurements on a Perkin Elmer TGA-7, FTIR spectra were recorded on a Mattson

Polaris spectrometer.

6-(methacrylamido)hexanoic acid) (8) **5**. To a solution of 6-aminocaproic acid (50 g, 0.38 mol) and NaOH (31 g, 0.77 mol) in water (150 ml), cooled to 0°C, methacryloyl chloride (50 g, 0.48 mol) was added dropwise cautiously, with stirring, over a 1.5 hour period. The temperature was kept below 5 °C. When the addition was complete the reaction mixture was allowed to reach room temperature and it was stirred for an additional hour. Then concentrated HCl was added until pH=3. The reaction mixture was extracted three times with $CHCl_3$. The $CHCl_3$ solution was dried over $MgSO_4$, filtered, and concentrated. The monomer (a clear oil) was crystallized from ethylacetate/petroleum ether at -20°C. Yield: 37,0 g (48.9%), mp. 48.5-50°C .
IR (KBr, cm^{-1}), 1697 (C=O, acid), 1651 (C=O, amide), 1535 (-NH); ^1H NMR (400 MHz, DMSO, δ in ppm): 1.20-1.60 ($m,6,C_3$, C_4, C_5-CH_2), 1.90 ($s,3,CH_3$), 2.20 ($t,2,C_2$-CH_2), 3.10 ($d,2,NHC\underline{H}_2$), 5.30 and 5.60 ($m,2,=CH_2$), 7.90 (s,1,NH), 11.95 (s,1,COOH); ^{13}C NMR (400 MHz, DMSO, δ in ppm): 18.59 (CH_3), 24.15, 24.24, 25.91, 28.71, 33.52 ($5xCH_2$ from spacer), 118.52 ($=\underline{C}(CH_3)CONH$), 140.04 ($CH_2=$), 167.25 (CONH), 174.35 (COOH);
Mass: 199 M^+, 154 M-COOH, 98 $CH_2=C(CH_3)C(=O)NH=CH_2^+$, 69 $CH_2=C(CH_3)C\equiv O^+$, $CH_2=CH(CH_2)_2CH_2^+$, 55 $CH_2=CHCH_2CH_2^+$.

11-(methacrylamido)undecanoic acid **6**, was synthesised similarly from 11-aminoundecanoic acid. The $CHCl_3$ extract gave a white solid after evaporation, which was recrystallized from ethanol/ether at -20°C. Yield (35%), mp. 62-65°C.
IR (KBr, cm^{-1}): 1702(C=O, acid), 1649(C=O, amide), 1532 (-NH); ^1H NMR (400 MHz, DMSO, δ in ppm): 1.20-1.60 ($m,16,C_3$-$C_{10}CH_2$), 1.85 ($s,3,CH_3$), 2.20 ($t,2,C_2CH_2$), 3.10 ($d,2,NHC\underline{H}_2$), 5.30 and 5.60 ($m,2,=CH_2$), 7.90 (s,1,NH), 11.90 (s,1,COOH); ^{13}C NMR (400 MHz, DMSO, δ in ppm): 18.62 (CH_3), 24.43 (2x CH_2), 26.37 (CH_2), 28.49 (CH_2), 28.68 (2x CH_2), 28.80 (CH_2), 28.87 (CH_2), 28.98 (CH_2), 33.61 (CH_2), 118.47 ($=C(CH_3)CONH$), 140.09 ($CH_2=$), 167.22 (CONH), 174.39 (COOH); Mass: 269 M^+, 98 $CH_2=C(CH_3)C(=O)NH=CH_2^+$, 69 $CH_2=C(CH_3)C\equiv O^+$, $CH_2=CH(CH_2)_2CH_2^+$, 55 $CH_2=CHCH_2CH_2^+$.

Modelreactions of bisketenimine 1 with nonanoic acid 2: These model reactions were carried out in dioxane or diglyme at various temperatures (80, 100, 130°C) and the >C=C=N IR absorption at 1993 cm^{-1} was monitored against time in a NaCl cell.
The reaction product **3** (mp. 110-115°C) was isolated by evaporating the solvent and washing the residue with petroleum ether (40/60). It was characterised by NMR and IR spectroscopy. Typical absorptions are: IR(KBr, cm^{-1}): 1693 and 1717 (imide C=O); ^1H NMR($CDCl_3$, δ in ppm): 7.3 (m,24,aromatic protons), 5.48 ($s,2,Ph_2C\underline{H}$), 2.68 ($t,4,CH_2C=O$), 1.55 and 1.23 (2xs,24,other CH_2), 0.86 ($t,6,CH_3$); ^{13}C NMR ($CDCl_3$, δ in ppm): 174.5 (C=O next to CH_2), 176.2 (C=O next to $CHPh_2$), 139.1 (Ar-N), 127.4 (other Ar in phenylenediamine), 128-138 (other Ar), 58.2 ($CHPh_2$), 22.6-38.7 (various CH_2), 14.1 (CH_3).

Synthesis of OH-functional and COOH-functional polymers: Hydroxyl functional copolymers were synthesized from 2-hydroxyethylmethacrylate, n-butylacrylate and methylmethacrylate using azobisisobutyronitril (1.5 mol%) as a radical initiator. Toluene was used as a solvent, the reaction temperature was 80°C. After the monomers were added, the reaction mixture was stirred for 16h and then poured into an excess of petroleum ether (40/60). The copolymer was purified by reprecipitation and dried in vacuum at 60°C. Yield 90%.
Carboxyl functional copolymers were prepared similarly from **4**, **5** and **6** with n-butylacrylate

and methylmethacrylate as comonomers, except for the use of a 1:3 mixture of toluene/isobutanol as a solvent. Yield 88% of reprecipitated copolymer. The copolymers were characterised by IR and NMR spectroscopy, the functional group content could be derived from ^{13}C NMR analysis: data of **P5** (CP-MAS, δ in ppm): 176.7 (-C(O)NH- and -C(O)OH, due to peak broadening, the absorptions are not clearly separated, 64.2 (OCH_2, BuA), 51.6 (OCH_3, MMA), 44.4 (CH_2NH-), 30,5 (CH_2, BuA main chain), 19.1 (γ-CH_2, BuA), 13.6 (CH_3, BuA).
Equivalent data were obtained for **P6**.

Crosslinking reactions: Crosslinked products were obtained by casting films of a mixture of prepolymer and crosslinker (bisketenimine **1** or freshly distilled MDI) from tetrahydrofurane solution in small teflon containers, and heating the films in an oven at various temperatures (80-130°C) for various periods (0-3h). Film thickness was about 80-100 μ.

Kinetic measurements: Samples were prepared by spin-coating a solution of a mixture of prepolymer and crosslinker on a KBr pellet. After evaporation of the solvent the pellet was mounted in a Specac thermostatic controlled cell. The desired temperature was reached within a few minutes, then the FTIR measurements were started. The relative absorbances were calculated in relation to the first measurement.

Dynamic mechanical measurements

Details on dynamic spring analysis (DSA) have been published previously (7). A steel spring was clamped at both ends with the aid of screw threads into a Rheonbron dynamic viscoelastometer. The prepolymer and crosslinker were applied with a brush from methylene chloride solution and the system was heated to the reaction temperature within 30 seconds. The measurements of tg δ against temperature for samples cured for various times at 100°C were done as quickly as possible to prevent further curing during the measurement. Since in this system film thickness is not known, relative rigidity is plotted against temperature rather than moduli E''/E'.

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