Polymer Bulletin 35, 9–16 (1995)

Polymer Bulletin

Crosslinking reactions with blocked carbodiimides

D. S. Tjin A-Lim [1], A. H. M. Schotman [2], R. Addink [1], K. te Nijenhuis [1], W. J. Mijs [1] *

[1] Delft University of Technology, Faculty of Chemical Technology and Materials
Science, Department of Polymer Technology, Julianalaan 136, 2628 BL Delft,
The Netherlands
[2] AKZO Research Laboratories, PO Box 9300, 6800 SB Arnhem, The Netherlands

Received: 14 December 1994/Accepted: 15 March 1995

Summary

Bis-4-(1',4'-phenylene)-5-phenyl-1,2,3,5-thiaoxadiazole-1-oxide **1**, a blocked bifunctional carbodiimide, has been used as a crosslinker for carboxyl functional poly(meth)acrylates. The thermolysis ("deblocking") reaction of **1** has been analyzed by FTIR spectroscopy. The crosslinking reaction has been simulated by using monofunctional model compounds. Intermediate compounds detected were thermally instable N-acylurea's decomposing into isocyanates and amides. Also some anhydride formation occurred. The final structure of the crosslinked product and the rates of crosslinking have been analyzed by FTIR and NMR spectroscopy. Modulus-M_c relations of networks based on carbodiimide compared with those based on bisketeneimine indicate thermolysis of crosslinks in the former case.

Introduction

In the course of our investigations on novel crosslinking reactions of carboxyl functional poly(meth)acrylates (1) we became interested in blocked carbodiimides as crosslinkers. Crosslinking with blocked hetero cumulenes is known in the case of polyisocyanates, applied in one component coating systems.

It is known that thermolysis of 4,5-diphenyl-1,2,3,5-thiaoxadiazole-1-oxide **3** yields diphenylcarbodiimide (2). Analogously, bifunctional 1,2,3,5-thiaoxadiazole-1-oxides yielding bifunctional carbodiimides should be able to act as "blocked" crosslinkers for carboxyl functional prepolymers.

Thus we have prepared **1** to study crosslinking reactions with carboxyl functional poly(meth)acrylates **2**. The monofunctional analogue **3** was synthesized as a model compound to simulate the crosslinking reaction, identifying intermediate and end products and analysing reaction rates.

Results and discussion

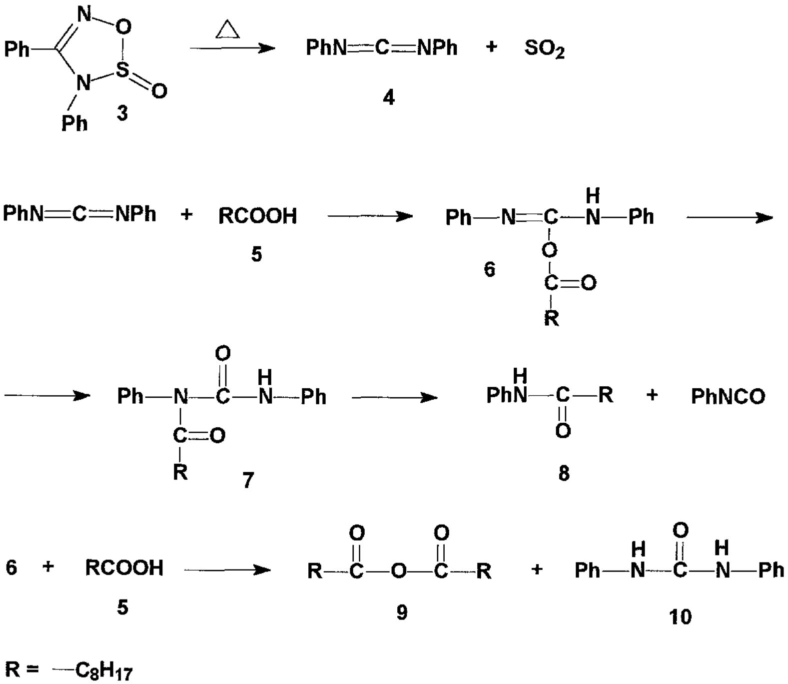
Model reactions

The model thermolysis reaction of **3** in the presence of nonanoic acid **5** is depicted in Scheme 1. The thermolysis product diphenylcarbodiimide **4** reacts further with **5** to the thermally instable N-acylurea **7**, which dissociates into phenylisocyanate and the amide **8**.

We have followed the reaction sequence from Scheme 1 with ^1H and ^{13}C NMR spectroscopy, putting the reactants **3** and **5** in a d_6-DMSO solution in the NMR tube, and recording spectra as a function of time at 90 °C. In table 1 representative NMR signals of **3** and **5** and their reaction products are collected. In the ^1H NMR spectra the appearance of typical NH peaks of the N-acylurea **7** at 11.38 ppm, strong at first, declining during the

---

* Corresponding author



Scheme 1. Thermolysis reaction of **3** in the presence of **5**

reaction and of the amide **8** at 9.82 ppm, weak at first, increasing during the reaction were clearly observed. Diphenylurea **10** also could be identified (NH at 8.68 ppm); **10** could result from reaction of carboxylic acid **5** with iminoester **6** as indicated in Scheme 1.

Table 1. Representative NMR signals of compounds **3** and **5** and their reaction products

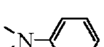
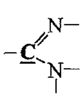
	$-\underline{C}H_2CO-$		>NH	 (para-H)	$-\underline{C}H_2CH_2CO-$	$>\underline{C}=O$	$>N-\underline{C}O-N<$	
	^1H	^{13}C	^1H	^1H	^{13}C	^{13}C	^{13}C	^{13}C
3	-	-	-	-	-	-	-	152.00
5	2.20	33.70	-	-	24.50	174.40	-	-
7	2.15	36.75	11.38	7.10	24.12	176.40	151.70	-
8	2.30	36.51	9.82	6.95	25.20	171.20	-	-
9	2.45	33.95	-	-	24.44	169.50	-	-
10	-	-	8.68	6.95	-	-	152.50	-

Table 2. Relative concentration of intermediates and products in the thermolysis reaction of **3** in the presence of **5** against time.

	20 min (90°)	40 min (90°)	120 min (90°)	120 min (100°)
Acid **5**	59%	39%	20%	17%
N-acylurea **7**	28%	38%	23%	3%
Amide **8**	9%	16%	52%	80%
Anhydride **9**	5%	8%	5%	-*)

*) In this experiment the anhydride slowly hydrolysed by the presence of H_2O in d_6-DMSO

Corresponding formation of anhydride **9** could also be confirmed: a triplet, coming up at 2.45 ppm (-CH_2-CO- well distinguishable from the analogous absorptions in the acid **5**, amide **8** or acylurea **7**), its intensity approximately remaining constant after about 20 min of reaction. It should be noted that both diphenylurea **10** and anhydride **9** could also be formed from phenylisocyanate and carboxylic acid **5** through an N-carboxyanhydride intermediate, which can react with another molecule of **5** to anhydride **9**, amine and carbon dioxide (3). Formation of intermediate **7**, gradually being converted into **8** and formation of **10** was also evident from the absorption of the para proton in the structure fragment  present in **7**, **8** and **10**. Initially two triplets emerged, arising from **7** and **10**, at 7.10 and 6.95 ppm respectively, but in the final product only a multiplet around 6.95 ppm is left, representing the partly overlapping signals of **8** and **10**.

Structure assignments of the reaction intermediates and products was further substantiated by ^{13}C NMR (Table 1). These spectra recorded during the model reaction represent the same pattern as the ^{1}H NMR spectra: **3** and **5** are converted into **8**, **9** and **10** as final products. The N-acylurea was again identified as an intermediate product. The ^{13}C absorptions at 152.56 from **3** and at 152.5 from **10** nearly overlapped, however the >C=O absorption of **7** at 151.7 could be clearly observed during the first stages of the reaction. The ^{13}C data of **7** and **10** were corroborated by those of authentic samples prepared from diphenylcarbodiimide and **5** and from phenylisocyanate and H_2O respectively (3).

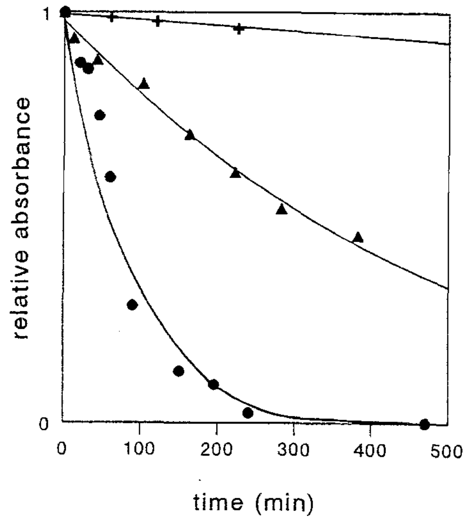
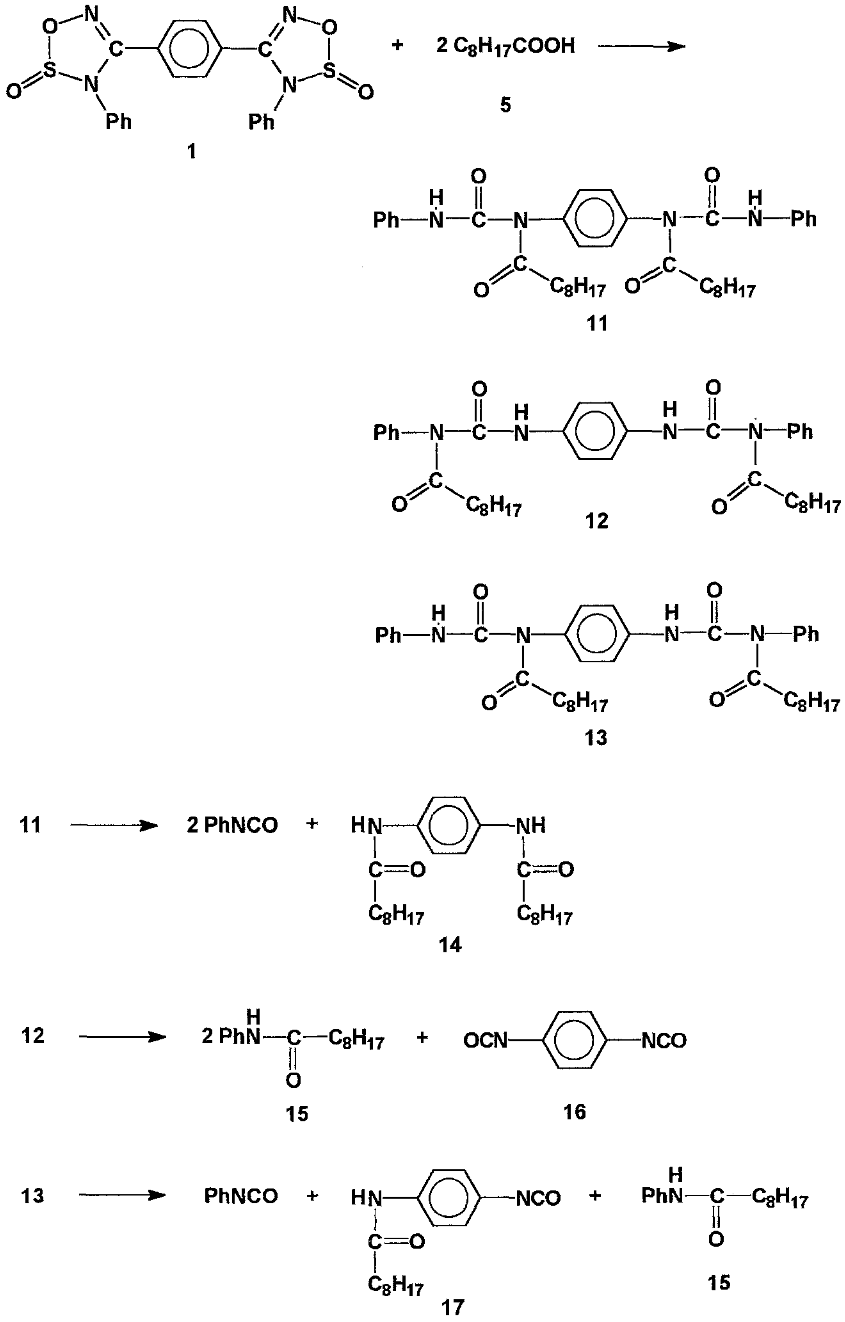


Fig. 1. Course of the reaction of n-nonanoic acid **5** with blocked biscarbodiimide **1** at + 60 °C, ▲ 80 °C and ● 100 °C.



Scheme 2. Formation and thermolysis of N-acylurea crosslink structures.

From the -CH_2CO- ^1H absorptions the relative course of the concentrations of intermediate and end products could be derived (Table 2). From these data it could be concluded that after 2 h at 100 °C formation of amide **8** from the N-acylurea intermediate **7** has been the main reaction (80%), whereas anhydride formation (about 8%) was a side reaction.

The reaction between the bifunctional blocked carbodiimide **1** and compound **5** (Scheme 2), simulating crosslinking is much more complicated. This reaction has been followed by FTIR spectroscopy (see fig. 1). The characteristic S=O stretching vibration at 1203 cm^{-1}, gradually disappearing, has been used to study the rate of thermolysis at various temperatures. From these graphs it is clear that the reaction needs at least a temperature of about 100 °C to go to completion in a reasonable time (5 h). The C=O stretching vibration at 1735 cm^{-1} naturally decreased during the reaction, gradually giving way to typical amide absorptions at 1594 and 1634 cm^{-1}. At 100°C also the slow rise and subsequent decline of small carbodiimide absorptions at 2118 and 2140 cm^{-1} and of the typical isocyanate peak at 2270 cm^{-1} were observed in the spectrum under the dry conditions used (refluxing dioxane). The latter peak was still present in the spectrum after 5 h.

The =C=N- double bonds are no longer equivalent in the reaction of **1** and **5** and consequently three types of addition products (**11**, **12** and **13**) to the various =C=N- bonds are formed (Scheme 2). Those should be the crosslink structures in the real network together with minor amounts of anhydride. The N-acylurea crosslinks dissociate into phenylisocyanate, 1,4-phenylenediisocyanate **16**, the amide substituted monoisocyanate **17** and the corresponding amides **14** and **15**. This occurs already at 100°C as is evident from the IR and NMR spectra recorded during the model reactions.

The dissociation into isocyanates **16** and **17** is connected with the breaking of crosslinks. Recording FTIR spectra of the crosslinking reaction of a carboxyl functional prepolymer with **1** at 120°C again showed the rise and decline of carbodiimide and isocyanate absorptions (see fig. 2). The disappearance of the isocyanate absorptions could be connected with evaporation of phenylisocyanate and 1,4-phenylenediisocyanate, but the isocyanate **17** can only disappear by becoming part of the network again or in a reaction with moisture. Theoretically crosslinks could also be restored by the reaction of **16** with COOH groups.

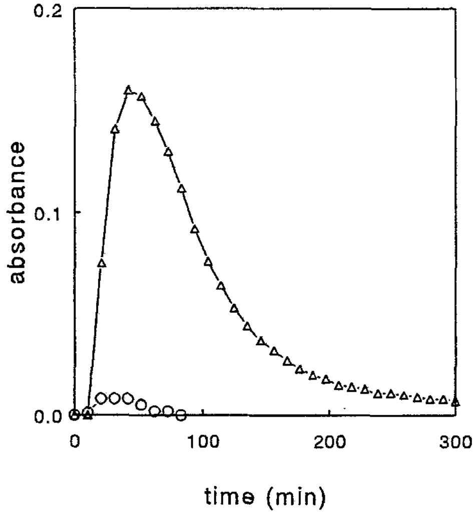


Fig. 2. Course of the IR absorption during crosslinking of prepolymer with blocked biscarbodiimide **1** at 120°C.
Δ 2270 cm^{-1}, isocyanate;
O 2118 and 2140 cm^{-1}, carbodiimide.

The question remains, what is the effect of the use of biscarbodiimide as crosslinker on the crosslinking density in a real network. Therefore, we prepared networks, under exactly the same conditions and stoichiometry, from a prepolymer with biscarbodiimide and bisketeneimine (1). The network obtained with bisketeneimine as crosslinker does not suffer from thermolysis of crosslinks.
We used the te Nijenhuis' model (4) which relates $\overline{M}_c$, the molar mass between crosslinks, with the equilibrium modulus (Young's modulus on the rubber plateau). This model is an extension of the statistical model of Flory and Stockmayer (5-9). Flory introduced a crosslinking index γ, which is defined as the average number of crosslinks per primary polymer molecule. The results obtained concerned tetrafunctional crosslinking of a monodisperse polymer. In the model of te Nijenhuis results are obtained for f-functional crosslinking of polydisperse polymers. Moreover, for various kinds of molecular weight distributions relationships were presented (4) between the equilibrium shear modulus of the network and the crosslinking index γ, the sol fraction w_s (i.e. the weight fraction of primary polymer not bound to the network) and the functionality f of the crosslinks. It is assumed that the distribution of the prepolymer used in this paper is a so called cumulative Flory distribution with $\overline{M}_w/\overline{M}_n>2$:

$$W(M) = \frac{\lambda}{\alpha} \left(e^{-\lambda M} - e^{-\mu M} \right) \tag{1}$$

$\lambda=1/\overline{M}_{n,0}$ $\mu= \lambda/(1-\alpha)$ where $\overline{M}_{n,0}$ is the value of $\overline{M}_n$ for $\alpha=0$
Parameter α follows from:

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{(\alpha-2)\ \ln(1-\alpha)}{\alpha} \tag{2}$$

The relationship between the equilibrium shear modulus and the network parameters reads:

$$\frac{G_e\ \overline{M}_n}{cRT} = 2(1-\alpha)\ [A(1-w_s^{0.5f})\ \frac{f-2}{f} - \frac{2(1-w_s)}{B}] \tag{3}$$

$$A = \frac{\alpha-2+\sqrt{\alpha^2+4(1-\alpha)/w_s}}{2(1-\alpha)z} \tag{4}$$

$$B = \frac{\dfrac{Az}{1+Az} - \dfrac{Az(1-\alpha)^2}{1+Az(1-\alpha)}}{\ln\dfrac{1+Az}{1+Az(1-\alpha)}} \tag{5}$$

$$z = (1 - w_s^{0.5f-1}) \tag{6}$$

$$\bar{\gamma}_w = A(2-\alpha) = \frac{\bar{M}_w}{\bar{M}_c} \tag{7}$$

If $\bar{M}_w$ and $\bar{M}_n$ of the primary polymer are known, then α can be calculated from Eq.2. Subsequently the weight average crosslinking index $\bar{\gamma}_w$ can be calculated from the equilibrium shear modulus with an iterative calculation process from Eqs. 3 to 6. Finally, the molecular weight between crosslinks can be calculated from the crosslinking index (Eq.7). Complete reaction of the prepolymer with a stoichiometric amount of crosslinker would give a M_c of 1300. However, the M_c calculated from the equilibrium moduli of the bisketeneimine and biscarbodiimide networks was 2480 and 5000 g/mol respectively. As the networks were prepared under exactly the same conditions and stoichiometry these values can be compared. Apparently 50% of the crosslinks in the final network based on biscarbodiimide are broken. The maximum amount of primary crosslinks that can be broken by thermolysis is, according to Scheme 2, 75%. This means that it is well possible that some repair of crosslinks from diisocyanate **16** and/or **17** has occurred.

Experimental

NMR spectra were recorded on a Varian VXR-400S or a Bruker AM 400 spectrometer. FTIR spectra were recorded on a Mattson Polaris spectrometer. Dynamic mechanical analysis in tensile mode was carried out on a Perkin Elmer DMA 7.

Carboxyl functional prepolymer was synthesised as described previously (1) Radical copolymerization of 58.5 mol% MMA, 31.3 mol% BuA and 10.1 mol% 6-(methacrylamido)-hexanoic acid yielded a precopolymer with M_n=16000, M_w= 41000, containing, according to titration, 0.77 mmol carboxylic acid groups per gram.

Bis-4-(1',4'-phenylene)-5-phenyl-1,2,3,5-thiaoxadiazole-1-oxide **1**, was synthesized according to literature (10) as the last step in the following sequence of intermediates: *terephtalaldehyde dioxime* (11); *terephtalodi(hydroxamoyl chloride)* (11, 12); *terephtalo-di(nitrile oxide)* (13).

4,5-diphenyl-1,2,3,5-thiaoxadiazole-1-oxide **3**, was synthesized according to literature (14) from benzohydroxamoyl chloride (12).

Modelreactions of blocked biscarbodiimide **1** *with nonanoic acid* **5** were carried out in dioxane at various temperatures (60, 80, 100 °C) and the S=O IR absorption at 1203 cm^{-1} was monitored against time.

Modelreactions of blocked carbodiimide **3** *with nonanoic acid* **5** were carried out in a d_6-DMSO solution in an NMR tube and the reaction was monitored at 90 and 100°C by ^1H and ^{13}C NMR.

Crosslinking reactions were carried out by casting films of a mixture of precopolymer with

0.385 mmol crosslinker, bisketeneimine or compound 1, per gram of prepolymer from tetrahydrofurane solutions, and curing the films in an oven at 130°C for 3 h. The mean value of the moduli at the rubber plateau, measured in tensile mode, were respectively $E=1.35\cdot10^6$ and $E=0.49\cdot10^6$ N/m^2 at 175°C . For the calculations of $\overline{M}_c$ the shear modulus $G_e=E/3$ was used.

A few drops of the THF solution were placed on a KBr pellet. After evaporation of the solvent, the pellet was placed in a thermostatically controlled cell, kept at 120°C, in the IR spectrometer. Then during 5 h every 10 min an IR spectrum was recorded.

Literature

1. Tjin A-Lim DS, Addink R and Mijs WJ (1994) Polymer Bulletin 32: 455
2. Wicks Z (1975) Prog in Org Coatings 3: 73
3. Schotman AHM (1993) PhD diss University of Technology, Delft.
   Schotman AHM (1991) Recl Trav Chim Pays Bas 110: 319
4. te Nijenhuis K (1991) Makromol Chem 192: 603; Makromol Chem Macromol Symp 45:117; (1993) Polym Gels Networks 1: 185 and 199
5. Flory PJ (1941) J Am Chem Soc 63: 3096
6. Flory PJ (1947) J Am Chem Soc 69: 30
7. Flory PJ (1953) Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, Chap IX
8. Stockmayer WH (1943) J Phys Chem 11: 45
9. Stockmayer WH (1944) J Phys Chem 12: 125
10. Eloy F and Lenaers R (1965) Bull Soc Chim Belges 74: 129
11. Overberger CG and Nelson RA Macromolecular Synthesis 5:21
12. Rajagopalan P, Advani BG and Talaty CN Org Synthesis V: 504
13. Iwakura Y, Akiyama M and Nagakubo K (1964) Bull Chem Soc Japan 37:767
14. Rajagopalan P and Advani BG (1965) J Org Chem 30:3369

Acknowledgement

Thanks are due to Mr. B. Norder (Dept. of Polymer Technology, TU Delft, The Netherlands) for his invaluable help in the DMA analyses.