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THERMAL BEHAVIOUR OF TRIGLYCIDYL-ISOCYANURATE (TGIC) IN THE PRESENCE AND IN THE ABSENCE OF POLYESTER

V. Vargha, S. Doszlop and O. Biró

TECHNICAL UNIVERSITY OF BUDAPEST, HUNGARY

Simultaneous thermal analysis and DSC measurements were used to characterize triglycidyl-isocyanurate as a technical product.

Triglycidyl isocyanurate (TGIC) is a crystalline polyepoxide compound suitable for the formulation of polyester or acrylic resin-based powder coatings. One of the greatest producers of TGIC is CIBA GEIGY, which distributes its product under the trade-name Araldite PT 810. TGIC was prepared at the Department for Plastics and Rubber Chemistry of the Technical University of Budapest. The thermal behaviour of this product was investigated by the use of simultaneous thermal analysis and DSC. Araldite PT 810 was used as a reference material for the investigations. The curing reaction of a saturated, carboxylated polyester, Uralac P2400 (a product of DSM Resins), with TGIC was also investigated by these two methods.

Experimental

Materials

Araldite PT 810; Supplier: CIBA GEIGY, Epoxy content: 9.3 val/kg, Epoxy equivalent weight: 107 g/equivalent, Melting point: 98°.

Uralac P2400; Supplier: DSM Resins, Acid value (ISO 3682): 30-37

Triglycidyl-isocyanurate (TGIC)

TGIC was prepared by reacting isocyanuric acid with an excess of epichlorohydrin in the presence of a catalyst, followed by dehydrochlorination. The final product was crystallized from methanol at room temperature. The insoluble part of the material (at the given mass ratio of methanol to

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final product of 1:1) was named the first fraction of crystallization (TGIC 1). After one day at room temperature, the separated crystals were filtered off and dried, and were named the second fraction of crystallization (TGIC 2). In a similar way, more crystallization fractions were collected (TGIC 3, 4, etc.). All fractions of crystallization were investigated separately. No essential difference was found after the second separation between the crystallization fractions. Therefore, one of them (TGIC 3) was selected for the thermal investigations. The first fraction of crystallization (TGIC 1) differs essentially from all other crystallization fractions of TGIC.

Basic characteristics:

TGIC 1

Appearance: white crystalline powder (needle-like crystals under the microscope)
Epoxy content: 10.1 val/kg
Epoxy equivalent weight: 99 g/equivalent
Melting point: 154°

TGIIC 3

Appearance: white crystalline powder (polygonal crystals under the microscope)
Epoxy content: 10.0 val/kg
Epoxy equivalent weight: 100 g/equivalent
Melting point: 100°.

Curing reactions

For the curing reactions, the saturated, carboxylated polyester resin Uralac P 2400 was used. The mass ratio of Uralac P 2400 to TGIC was 93:7, as suggested in the literature [1]. The two components were mechanically rubbed together. The reactions were investigated by simultaneous thermal analysis and by DSC. DSC was performed under isothermal conditions at 180°, the suggested reaction temperature.

Simultaneous thermal analysis

Measurements were made with a Derivatograph C supplied with a microprocessor. TG, DTG and DTA curves were registered at a heating rate of 5 deg/min.

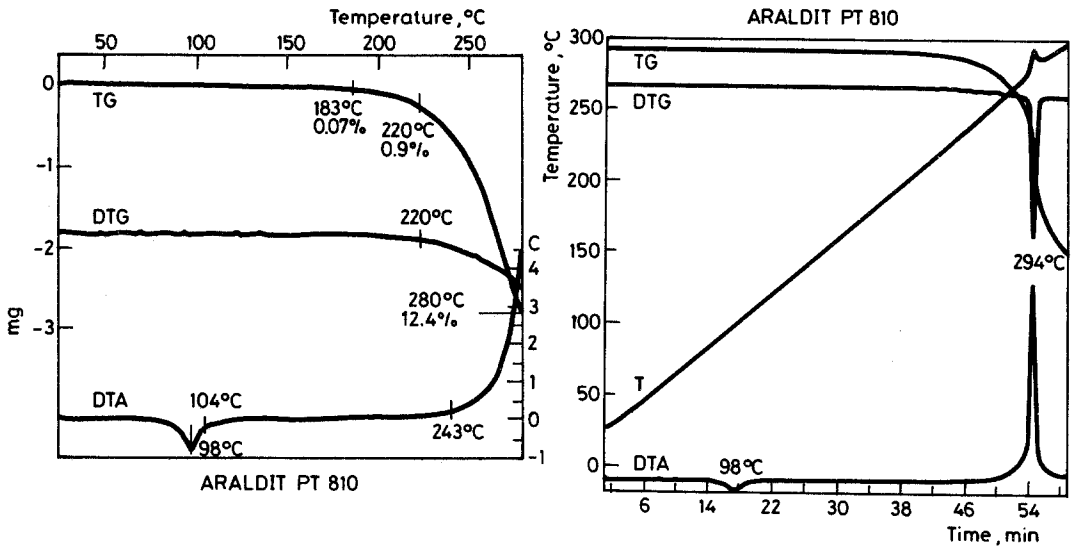
DSC measurements

DSC measurements were made with a Perkin Elmer 2 DSC instrument. Results are also given for measurements made earlier at the German Institute of Plastics (Deutsches Kunststoff-Institut Darmstadt) with a Du Pont 2100 instrument [2].

Results

Testing TGIC as a function of storage time

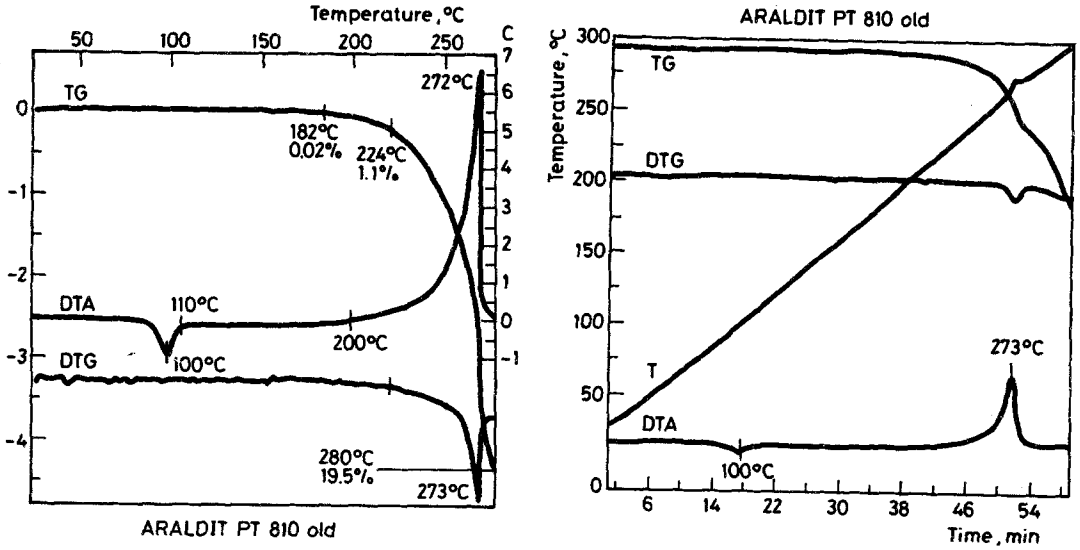
Simultaneous thermal analysis was used to test the quality of TGIC depending on the time of storage. Figures 1-4 show that both the temperature and the heat of decomposition of a fresh sample are higher than those of a sample after storage for 2 years.



Figs 1-2 A fresh sample of "Araldite PT 810" tested by simultaneous thermal analysis

Testing TGIC after preparation

The fractions of crystallization were investigated by simultaneous thermal analysis and DSC after preparation. Figure 5 shows the thermoanalytical curves of fraction TGIC 1. Figure 6 refers to third fraction TGIC 3.



Figs 3-4 "Araldite PT 810" tested by simultaneous thermal analysis after two-year storage

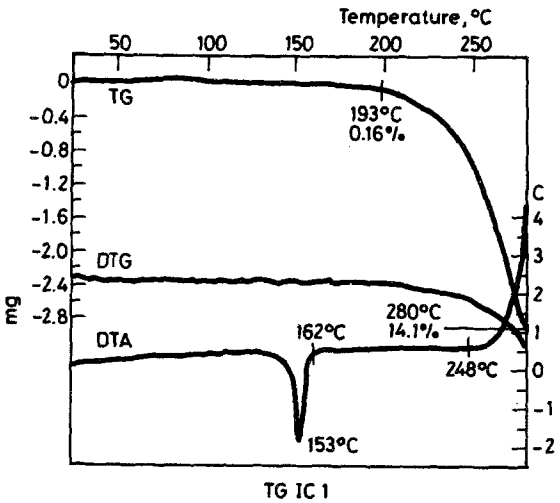


Fig. 5 First crystallization fraction of TGIC (TGIC 1) tested by simultaneous thermal analysis

TGIC 1 differs essentially from TGIC 3 as it has a higher melting point, i.e. 153° *vs.* 100°. Thermoanalytically, no difference was found in the crystallization fractions after separation of the first fraction.

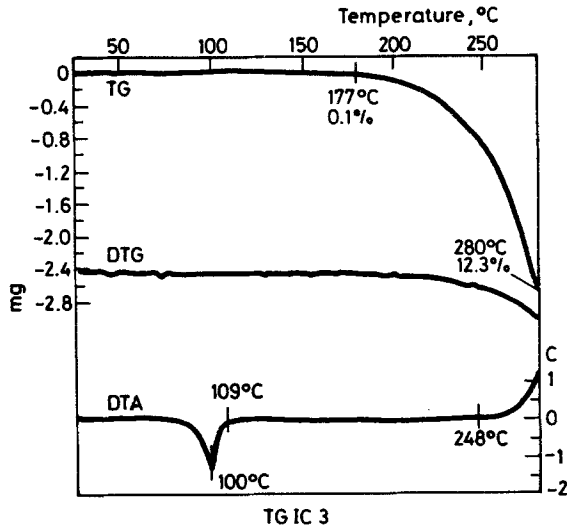


Fig. 6 Third crystallization fraction of TGIC (TGIC 3) tested by simultaneous thermal analysis

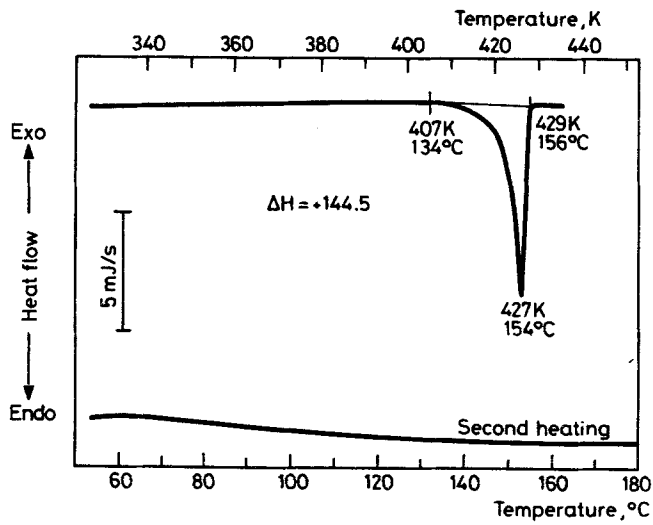


Fig. 7 First crystallization fraction of TGIC (TGIC 1) tested by DSC Perkin Elmer 2

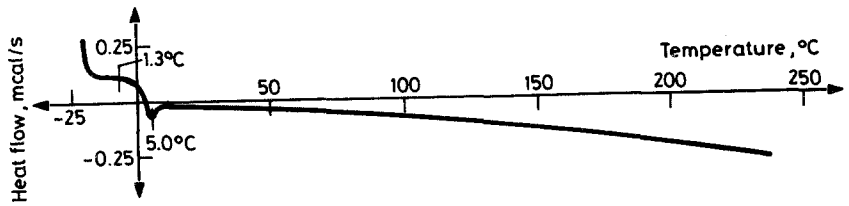


Fig. 8 First crystallization fraction of TGIC (TGIC 1) in amorphous state tested by DSC Du Pont 2100

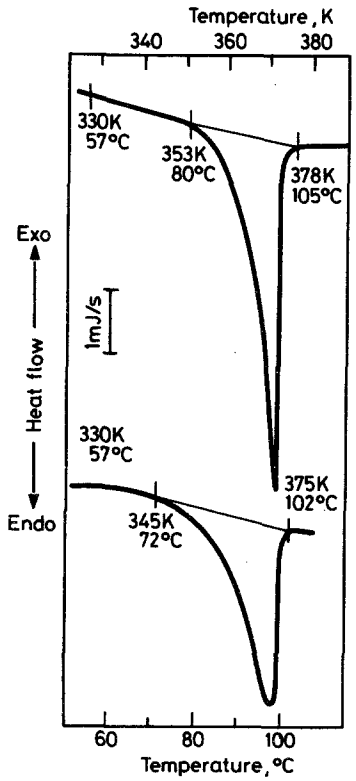


Fig. 9 Third crystallization fraction of TGIC (TGIC 3) tested by DSC Perkin Elmer 2

The DSC measurements correlate with those of simultaneous thermal analysis (Fig. 7-9). The DSC curves of the fraction TGIC 1 can be seen in

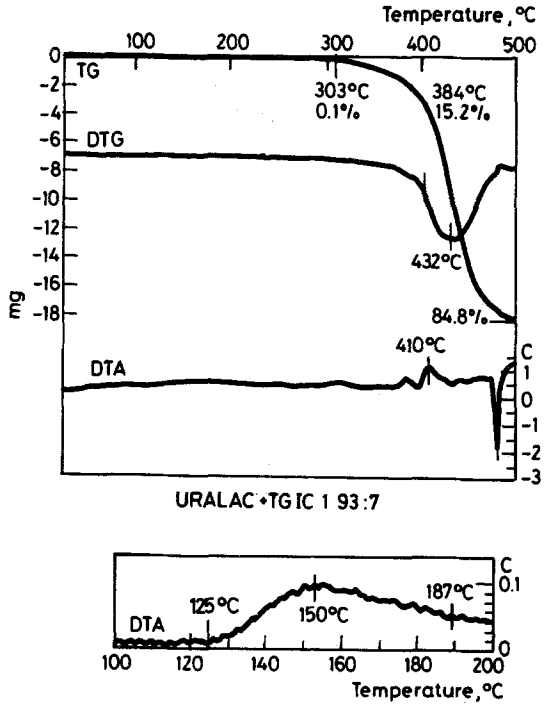


Fig. 10 Reaction between "Uralac P2400" and TGIC 1 detected by simultaneous thermal analysis

Fig. 7. The first fraction has a sharp melting peak at 154°, with a melting enthalpy of +144.5 J/g. No recrystallization takes place after slow cooling, even after storage for one month at room temperature or at 5°. According to the earlier measurements with the DSC Du Pont 2100 instrument, the glass transition temperature of the amorphous state of TGIC 1 was 5° ([2], Fig. 8). It was found that all other fractions of crystallization behave similarly in the amorphous state.

Figure 9 shows the DSC curves of the fraction TGIC 3. The melting point is 100, and the melting enthalpy is +88.9 J/g. This fraction does not recrystallize after slow cooling, but recrystallization occurs after storage for one day at room temperature. It can be seen in Fig. 9 that the melting point is lower (98° *vs.* 100°) and the melting enthalpy is less (+72.4 J/g *vs.* +88.9 J/g) after recrystallization. The yield of crystallinity relating to the former state is 81.4%. This fact has consequences concerning the output of the crystalline product during manufacture.

Testing the curing reaction of Uralac P2400 with TGIC

The effect of the heat of the curing reaction could hardly be detected by using simultaneous thermal analysis (Fig. 10). The higher decomposition temperature for the reaction mixtures (Figs 10-12) than that for the pure polyester (Fig. 13) points to the fact that a reaction took place between the two components.

Because of its low sensitivity, simultaneous thermal analysis did not prove a suitable method for following the heat effects of the curing reaction between the polyester and TGIC.

For detection of the heat effects of the curing reaction beetwen the two components, DSC measurements were also made under isothermal conditions at 180° (Figs 15-17). The curing process could be followed as a reaction with a monotonously decreasing rate. A transient time (τ_{tr}) of 1 min was established for ensuring the isothermal conditions. Although the curing reaction already begins during this period, the reaction time (τb) and enthalpy (ΔH) could be estimated. The time of curing found by DSC in each case correlated with the time of stoving suggested in the literature [3]. The end of the glass transition range for the cured systems ($T_{g\ end}$) was also es-

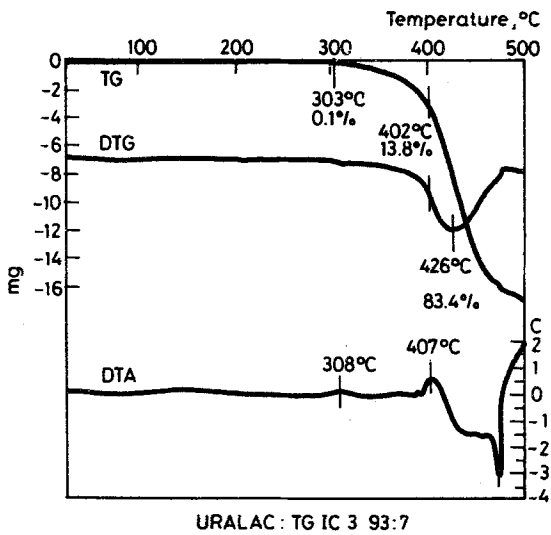


Fig. 11 Reaction between "Uralac P2400" and TGIC 3 followed by simultaneous thermal analysis

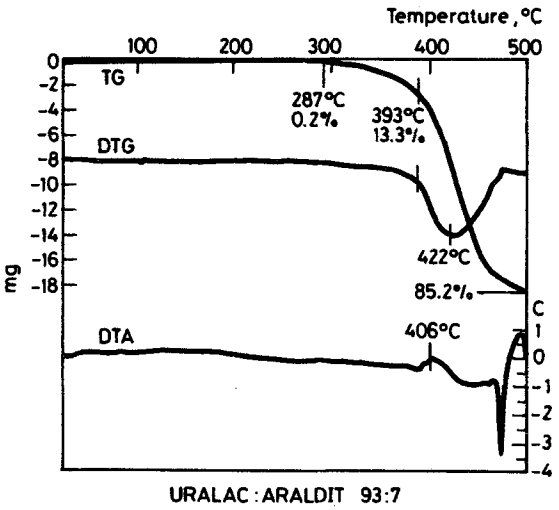


Fig. 12 Reaction between "Uralac P2400" and "Araldite PT 810" tested by simultaneous thermal analysis

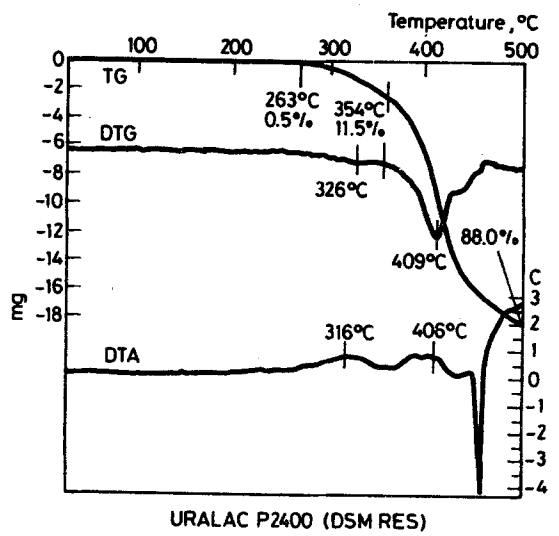


Fig. 13 Thermal behaviour of "Uralac P2400" tested by simultaneous thermal analysis

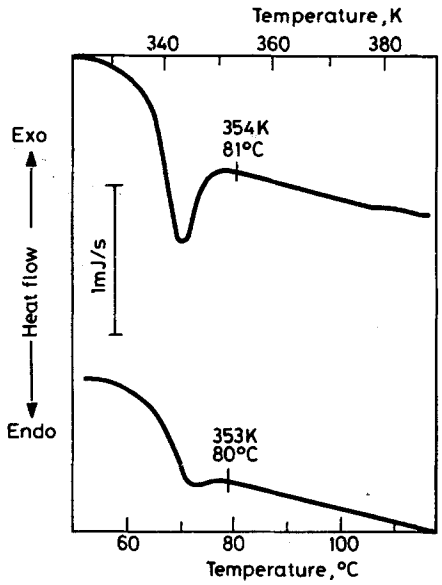


Fig. 14 Thermal behaviour of "Uralac P2400" tested by DSC Perkin Elmer 2

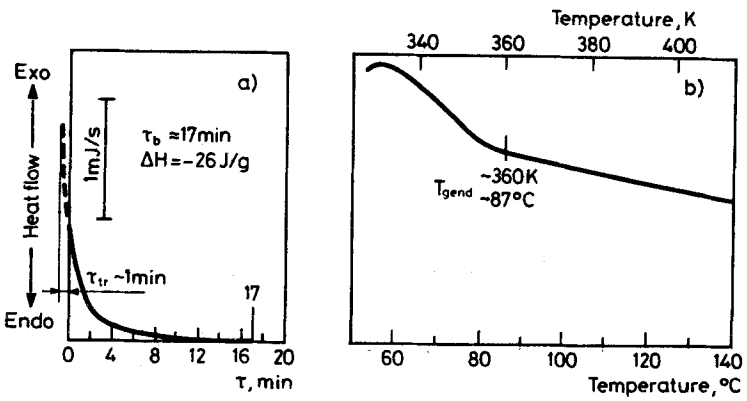


Fig. 15 a) Reaction between "Uralac P2400" and TGIC 1 followed by DSC Perkin Elmer 2 at 180°C, b) DSC curve of the cured system

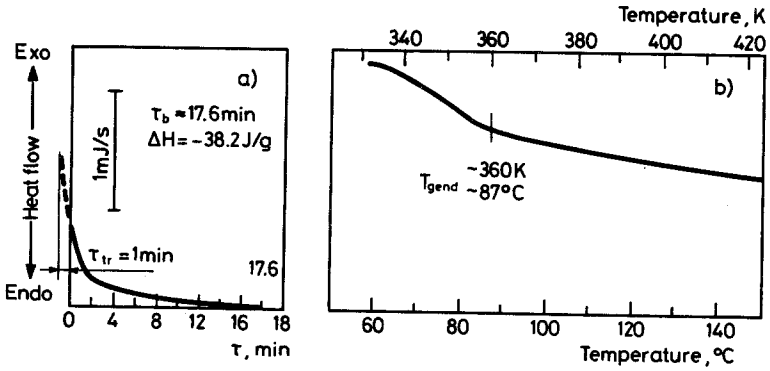


Fig. 16 a) Reaction between "Uralac P2400" and TGIC 3 followed by DSC Perkin Elmer 2 at 180°C, b) DSC curve of the cured system

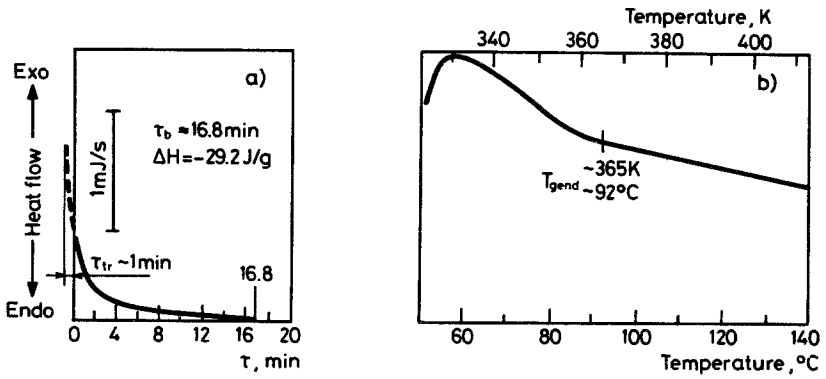


Fig. 17 a) Reaction between "Uralac P2400" and "Araldite PT 810" followed by DSC Perkin Elmer 2 at 180°C, b) DSC curve of the cured system

timated, and was found in all cases to be higher than that of the pure polyester (Fig. 14).

Conclusion

Simultaneous thermal analysis and DSC measurements were used to characterize triglycidyl-isocyanurate as a technical product and as the fractions of crystallization after manufacture.

Simultaneous thermal analysis did not, but DSC proved to be a suitable method for detecting and characterizing the curing reaction of a polyester with triglycidyl-isocyanurate.

* * *

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References

1 DSM Resins: Data Sheet Uralac P2400.
2 D. Braun, V. Vargha, Angew. Makromol. Chem., 173 (1989) 219.
3 CIBA GEIGY: Data Sheet Araldite PT 810.

Zusammenfassung – Zur Beschreibung von technischem Triglycidyl isocyanurat wurden simultane Thermoanalyschen- und DSC-Untersuchungen durchgeführt.