On the physical crosslinking of amine-extended polyurethane urea elastomers:
A crystallographic analysis of bis-urea from diphenyl methane-4-isocyanate and 1,4-butane diamine*)**)

L. Born and H. Hespe

Zentrale Forschung und Entwicklung (Central Research and Development), Bayer AG, Leverkusen, West Germany

Abstract: The substance under investigation is taken as a model for hard segments consisting of MDI[1]) and 1,4-butane diamine. It crystallizes in the triclinic space group P $\bar{1}$ with a = 4.6297; b = 5.8259; c = 25.286 Å; α = 90.721; β = 91.580; γ = 102.90 degrees and Z = 1. Bond distances and angles are given, together with some data on the conformation.

The most significant finding is that neighbouring molecules in one and the same plane are linked to one another by means of bifurcated hydrogen bonds.

A comparison with the corresponding data for an analogous bis-urethane provides a plausible explanation of the main differences between diamine and glycol extension in polyurethane elastomers.

Key words: Polyurethane elastomers, hard segment, crystal structure.

1. Introduction

It has been known for some time that polyurethane elastomers with diamines as chain extenders retain their elastic properties up to very much higher temperatures than is the case with polyurethane elastomers which are produced using diols. The reduction in the modulus of elasticity brought about by increasing temperature is also much less with amine-extended products. In many cases there is even an increase in the modulus — a feature which is also typical of chemically crosslinked elastomers (fig. 1).

The greater heat stability of hard segments of diisocyanates and diamines is exploited, for example, in the production of elastic fibres with very short hard segments, which yield elastic products having excellent recovery. Experience shows that replacing the diamine by a glycol, while otherwise leaving the formulation unchanged, leads to plastic products which cannot be used for the production of elastic fibres.

For many fields of application, a mayor disadvantage of amine extension is that the elastomers frequently lack thermoplastic processability.
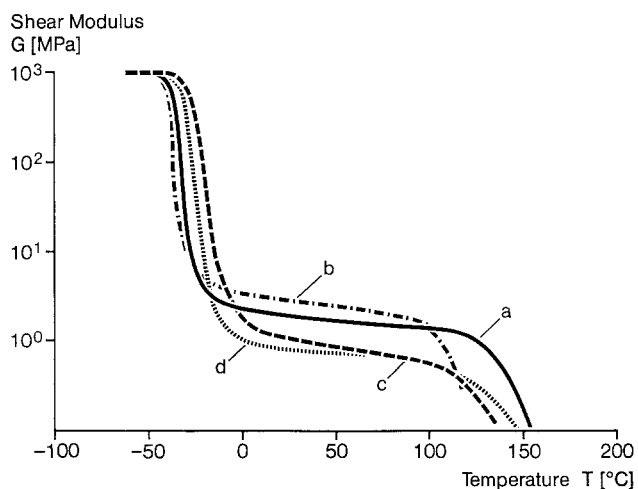

Fig. 1a. Shear modulus of polyurethane elastomers with different hard segments; a: 1,5-naphthylene diisocyanate + 1,4-butanediol; b: 1,6-hexamethylene diisocyanate + 1,4-butanediol; c: 4,4'-diphenylmethane diisocyanate + 1,4-butanediol; d: MDI + hydroquinone bis(2-hydroxyethyl)ether; Soft segment of all samples: (ethylenglycol/butanediol)adipate
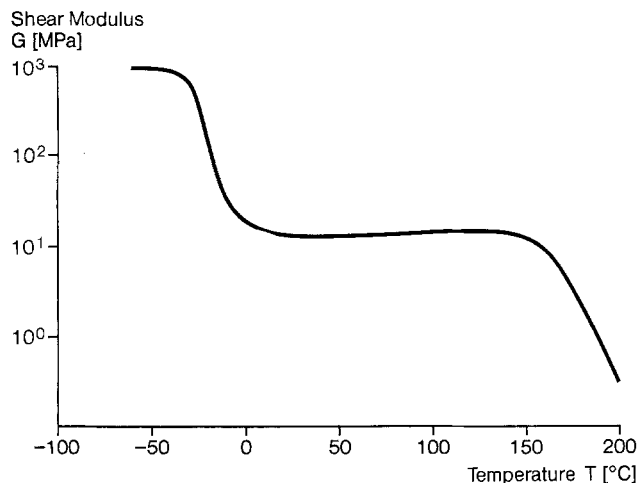

Fig. 1 b. Shear modulus of an amine-extended elastomer; hard segment: MDI + aromatic diamine; soft segment: as in figure 1 a

Table 1. Crystallographic data

Substance	bis-urea	bis-urethane
Molecular formula	$C_{32}H_{34}N_4O_2$	$C_{32}H_{32}N_2O_4$
Molecular weight (g/mol)	506.65	508.624
Crystal system	triclinic	monoclinic
Space group	$P\,\bar{1}$	$P\,2_1/b$
Lattice constants (Å)	$a = 4.6297$	5.1031
	$b = 5.8259$	6.7354
	$c = 25.2861$	39.628
Lattice constants (degree)	$\alpha = 90.721$	85.948
	$\beta = 91.580$	90.0
	$\gamma = 102.900$	90.0
Cell volume (Å³)	$V = 664.4$	1358.7
Molecules per cell	$Z = 1$	2

The aim of this paper is to explain the reason for these differences in behaviour by means of crystallographic analysis of a bis-urea which serves as a model for a hard segment consisting of MDI and 1,4-butane diamine. For purposes of comparison, the results of previous analyses on a bis-urethane are quoted [1, 2].

2. Experimental section

The model substance under investigation is a bis-urea produced by reacting diphenyl methane-4-isocyanate with 1,4-butane diamine. It was produced in the same way as the bis-urethane which is described in greater detail in [2].

The structural formula is shown below:
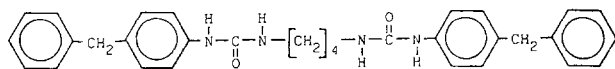
Crystals of sufficient size were obtained from a DMF solution. The quality of the crystals used was checked by means of some Weissenberg and rotating crystal photographs which also provided initial information on the symmetry of the crystals. The six lattice parameters and the reflection intensities were determined on a CAD 4 four-circle diffractometer (from Enraf-Nonius), coupled on-line to a PDP-11/23 computer, with 25 reflection positions being located, centred and indicated. In view of the symmetry of the space groups, and the number of molecules per cell, it was only necessary to determine the atomic coordinates of one half of the molecule.

Direct methods [3] were used to determine the structure. The urea, phenyl and phenyl methyl groups have been introduced into the calculation of the normalized structure factors (E-values). The 320 largest of them yielded 4,703 phase relationships, of which 4,395 were used. Further details, together with the atomic coordinates, are to be published in a separate paper.

3. Results and discussion

In the following section, the results of this analysis are set out and compared with the corresponding data of the analogous bis-urethane of diphenyl methane-4-isocyanate and 1,4-butane diol, which was the subject of a previous investigation.

From table 2 it is clear that the bond distances do not differ noticeably from the values given in the literature. The only difference is that the $C = O$ double bond is slightly extended unlike that of the bisurethane. In the urea group, the $N - C$ bond distance adjacent to the phenyl ring is 0.03 Å larger than the normal value for urea. The reason for this is probably the bonding of this nitrogen atom to a further atom (an aromatic C (sp^2) atom). Apart from the $C = O$ double bond, there are no appreciable differences between the bis-urethane and the bis-urea as far as bond distances are concerned.

The bond angles of the bis-urea also correspond broadly to the values given in the literature. In most cases the bond angles of the bis-urethane are smaller, which also agrees with the literature. The very small angle at the carbon atom of the carbonyl group (110.3 °) can be explained, according to Gillespie [4], by the pressure of the double bond on the neighbouring single bonds. The tetrahedron angle at the central C-atom of the diphenyl methane group is clearly enlarged. The slight differences between the bis-urea and the bis-urethane should not be overestimated, because the outer benzene ring is subjected to strong thermal motions, which reduce accuracy when determining its atomic coordinates.

In addition to the benzene rings, the urea group and the chain extender sequence $N - (CH_2)_4 - N$ can be termed largely "planar", and as such are completely analogous to the corresponding structural features of

Table 2

	Bond Distances (Å)		Bond Angles	
	urea	urethane	urea	urethane
d (C=O)	1.238	1.215		
	1.526	1.518		
			114.49°	111.3°
	1.509	1.498		
			111.61°	107.5°
	1.454	1.444		
			120.61°	115.5°
	1.388	1.344		
			116.23°	110.3°
	1.363	1.342		
			124.25°	126°
	1.415	1.418		
			113.8°	115°

For the bis-urethane the N_2H_2 group has to be substituted by Oxygen

bis-urethane. Table 3 shows the angles between some of the "best planes".

Table 3. Angles between the best planes

	bis-urea	bis-urethane
Phenyl (outer)/phenyl (inner)	72.2	85.5
Phenyl (inner)/N−CO−N	45.4	
Phenyl (inner)/N−CO−O		27.6
N−CO−N /N−(CH$_2$)$_4$−N	6.5	
N−CO−O /O−(CH$_2$)$_4$−O		9.6

This comparison shows two remarkable discrepancies: the angle between the two phenyl rings is considerably smaller in the case of the bis-urea, while the angle between the inner phenyl ring and the neighbouring urea group is considerably greater than the corresponding angle with bis-urethane.

Figure 2 shows the arrangement of adjacent molecules linked together by hydrogen bonds, while figure 3 shows the corresponding positions of adjacent molecules which are not linked by hydrogen bonds.

It can be seen from figure 2 that, with bis-urethane and with bis-urea, a planar system of hydrogen bonds exists. Contrary to Bonart's earlier ideas [5], however,
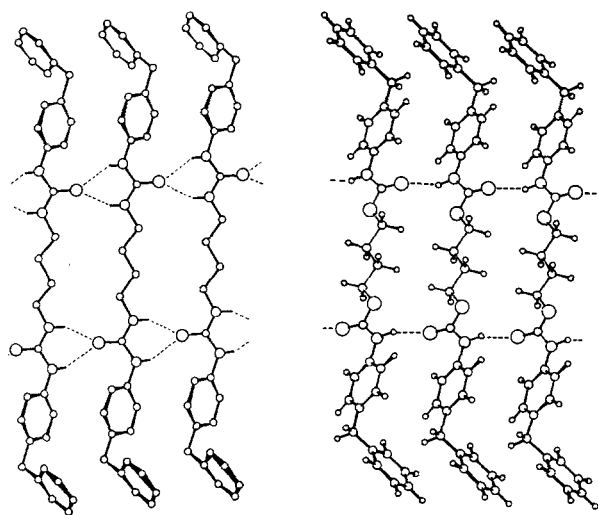
Fig. 2. Arrangement of adjacent molecules, with hydrogen bonds in the drawing plane; a: bis-urea; b: bis-urethane

Fig. 3. Arrangement of adjacent molecules, with hydrogen bonds perpendicular to the drawing plane; a: bis-urea; b: bis-urethane

bis-urea in fact features two bifurcated hydrogen bonds; in other words each carbonyl oxygen is bonded to both the N−H dipoles of the opposite urea group. This statement is substantiated by the heteromolecular distances given in table 4.

The practically symmetrical arrangement of the carbonyl oxygen between the two N−H protons of the adjacent molecule, and the stronger interaction between adjacent molecules in the bifurcated hydrogen bonds lead to a noticeably tighter packing of the chains (cf. the $C_1 - C_1'$ distances). As a result of this, the dis-
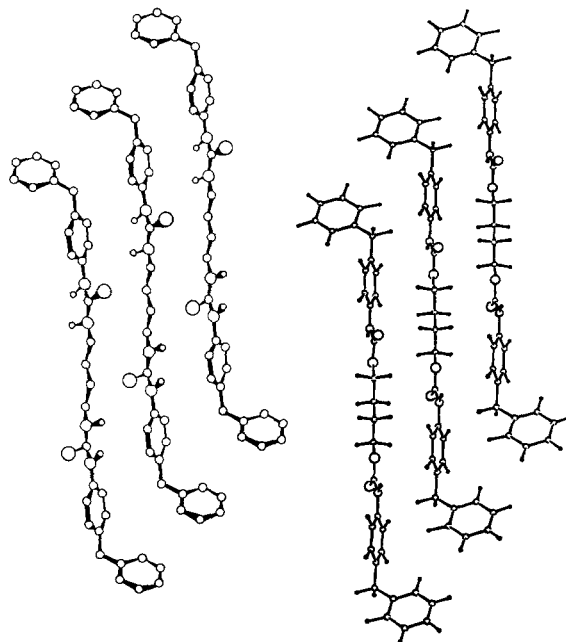
tance between the two adjacent phenyl rings is also reduced. The tighter packing of the phenyl rings is made possible by a greater inclination towards the associated urea group (45.4° with bis-urea compared with 27.6° with bis-urethane; cf. table 3).

The increase in the C=O bond distance with bis-urea (cf. table 2) is due to the influence of the neigh-

Table 4. Heteromolecular distances

	bis-urea	bis-urethane
$C_1 - C_1'$	4.63 Å	5.10 Å
$C_1 - O_2$	3.39	3.94
$H_1 - O_2$	2.27	2.08
$H_3 - O_2$	2.14	
$N_1 - O_2$	2.96	2.98
$N_3 - O_2$	2.88	

bouring N—H groups. From the available data, however, it is not possible to infer the extents to which a) the intra-molecular influences and b) the inter-molecular influences contribute to this effect. Supplementary IR and DSC measurements were therefore carried out.

IR measurements

A Digilab FTS 15 E Fourier Transform Spectrometer was used for these measurements. The two substances were measured both in crystalline form and dissolved in DMSO. The crystals were examined using the FMIR method with a germanium crystal. In the case of bis-urethane, the concentration of the solution was 10 mg/ml, while with bis-urea the solution was saturated. The irradiated layer was 0.2 mm thick. In both cases the spectrum of the solvent was subtracted.

Figures 4 a and 5 a show the spectra of the two model compounds in the crystalline state, and figures 4 b and 5 b show the spectra of the solutions. The wave numbers of the C=O stretching vibration are given in table 5.

Even in solution, the wave number (frequency) of this stretching vibration is less with bis-urea than with bis urethane, a fact which is contributable to the influence of the neighbouring N—H groups within a molecule, and perhaps also to interaction with the solvent. The transition to the crystalline state causes the band to shift by 68 cm^{-1} in the case of bis-urea, i. e. by more
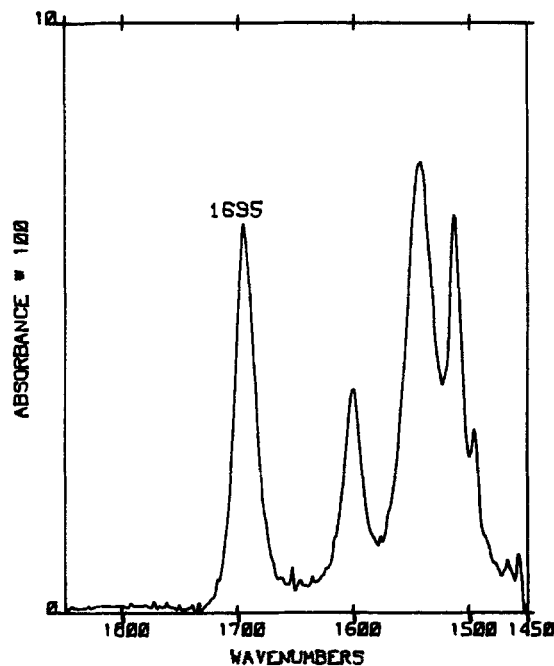
than twice as much as with bis-urethane. This effect must be attributed to the stronger interaction between the molecules of the bis-urea.

Fig. 4 b. Infrared spectrum of bis-urea, dissolved in DMSO (DMSO spectrum subtracted)
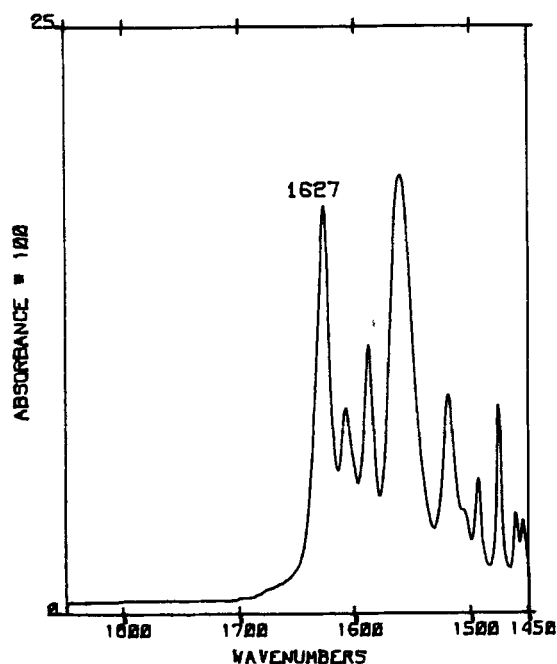

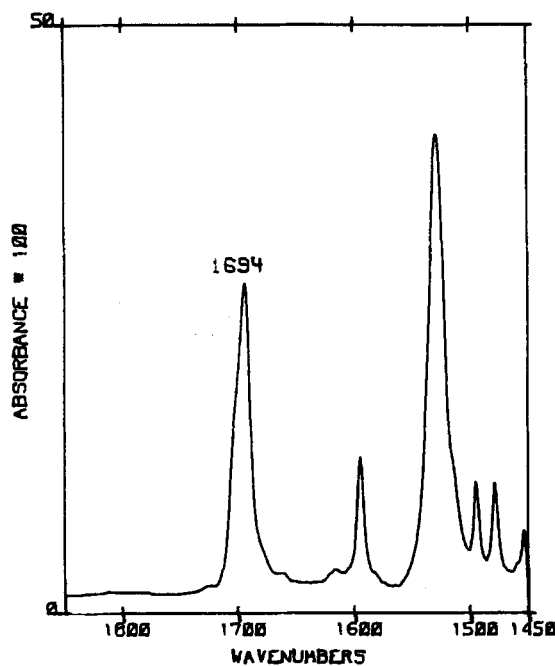Fig. 4 a. Infrared spectrum of bis-urea crystals

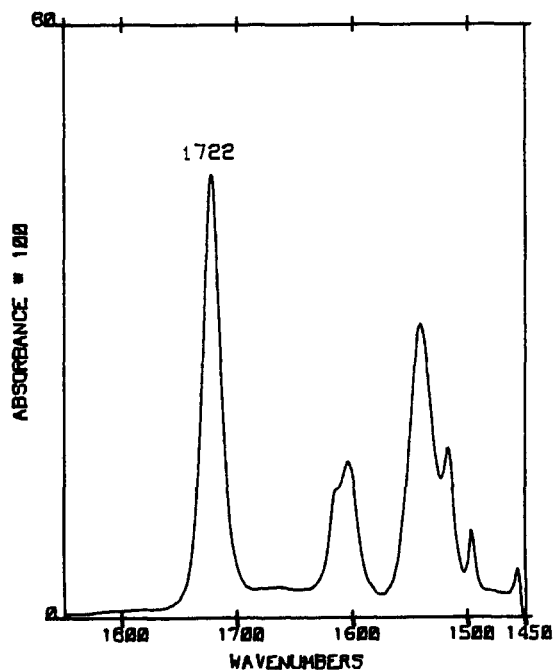

Fig. 5 a. Infrared spectrum of bis-urethane crystals

Fig. 5 b. Infrared spectrum of bis-urethane, dissolved in DMSO (DMSO spectrum subtracted)

Table 5. Wave numbers of the carbonyl stretching vibration

| | $\lambda_{C=O}$ (cm^{-1}) | | |
	Crystal	Solution	$\Delta\lambda$
bis-urea	1,627	1,695	68
bis-urethane	1,694	1,722	28

Differential scanning calorimetry

The Perkin-Elmer DSC-2 was employed, using standard aluminum sample pans. The heating rate was 20 K/min, and the sample mass 1 mg. All the measurements were conducted under nitrogen.

Figure 6 shows the DSC diagrams obtained. Table 6 lists the values for melting temperature T_m, latent heat of fusion ΔH and entropy of fusion ΔS which were determined.

Table 6. Thermal data

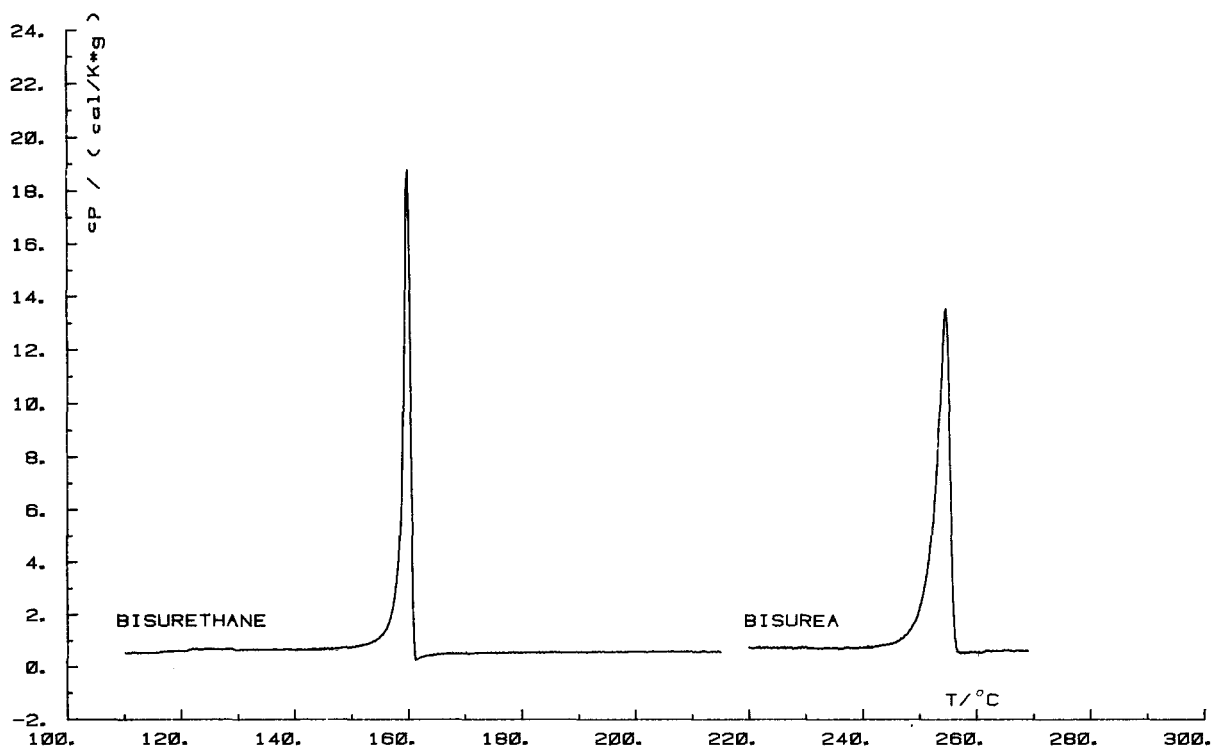| | T_m | | ΔH (cal/g) | $\Delta S \left(\dfrac{cal}{g \cdot K}\right)$ |
	°C	K		
bis-urea	254	527	40.5	$7.7 \cdot 10^{-2}$
bis-urethane	161	434	31.4	$7.2 \cdot 10^{-2}$

Fig. 6. DSC scans of bis-urea and bis-urethane; heating rate: 20 K/min; sample mass: 1 mg

It is clear that the entropy of fusion is practically the same for both compounds, which was to be expected in view of their very similar structures. The higher melting point of the bis-urea is therefore due mainly to the greater interaction energy between the molecules (latent heat of fusion). This finding confirms the conclusions reached on the basis of the IR spectra.

4. Concluding remarks

The most important finding here is the appearance of the bifurcated hydrogen bonds, and the strong interaction which results between neighbouring urea groups in the crystal. This accounts for the greater heat stability of the bis-urea crystals compared with those of the corresponding bis-urethane.

Analogous effects can also be observed when comparing the hard segments in amine and glycol-extended segmented elastomers. With the former, the melting temperature of the hard segments is frequently so high that they cannot be melted without decomposing. To sum up, therefore, it can be said that amine-extended elastomers, as a result of the extremely strong interaction of their hard segments, fill the gap between classical thermoplastic elastomers and chemically crosslinked rubber.

References

1. Born L, Hespe H, Crone J, Wolf KH (1982) Coll & Pol Sci 260:819
2. Born L, Crone J, Hespe H, Müller EH, Wolf KH (1984) J Pol Sci-Pol Phys Ed 22:163
3. Main P et al (1978) Multan 78, a System of Computer Programs for the automatic Solution of Crystal Structures from X-Ray Diffraction Data, Universities of York and Louvain
4. Gillespie RJ (1963) J Chem Educ 40:295
5. Bonart R (1968) J Macromol Sci B2:115, Bonart R, Morbitzer L, Rinke H (1970) Koll Z, Z Polymere 240:807, Bonart R, Morbitzer L (1970) Koll Z, Z Polymere 241:909

Authors' address:

Dr. H. Hespe
Bayer AG, ZF-TPE-Polymerphysik
D-5090 Leverkusen, Bayerwerk