University of Groningen

Determination of polybutylene terephthalate polycondensation equilibrium constant using a batch reactor

Darda, Pranay Jairam; Hogendoorn, Kees; Molenkamp, Tjaart; Versteeg, Geert

Published in:
Macromolecular Symposia

DOI:
[10.1002/masy.200450222](https://doi.org/10.1002/masy.200450222)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2004

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Darda, P. J., Hogendoorn, K., Molenkamp, T., & Versteeg, G. (2004). Determination of polybutylene terephthalate polycondensation equilibrium constant using a batch reactor. *Macromolecular Symposia*, 206(1), 275-289. <https://doi.org/10.1002/masy.200450222>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Determination of Polybutylene Terephthalate Polycondensation Equilibrium Constant Using a Batch Reactor

Pranay Jairam Darda,¹ Kees Hogendoorn,¹ Tjaart Molenkamp,[‡] Geert Versteeg^{1*}

¹ Design and Development of Industrial Processes, Faculty of Chemical Technology,
University of Twente, P. O. Box 217, 7500 AE, Enschede, The Netherlands
E-mail: g.f.versteeg@ct.utwente.nl

[‡] Department of Performance Materials – Chemistry & Technology, DSM Research, P.O.Box 18, 6160 MD, Geleen, The Netherlands

Summary: The PBT polycondensation equilibrium constant at 255 °C was determined using a batch reactor. Starting from a Polybutylene terephthalate (PBT) prepolymer having a degree of polymerisation of 12.7, equilibrium experiments were performed in the range of 1 to 50 mbar. The equilibrium degree of polymerisation (i) was determined indirectly using dilute solution viscometry of a solution of 1 weight % PBT in *m* – cresol. The degree of polymerisation of PBT obtained at equilibrium in the range of 1 to 50 mbar at 255 °C as a function of the BDO partial pressure (mbar) could be expressed by: $i = 111.47 - 86.18 \exp(-1.14 P_{\text{BDO}}^{-1.44})$. The equilibrium solubility of 1,4 butanediol (BDO) in the PBT melt was derived from the BDO partial pressure using the Flory – Huggins theory. The PBT polycondensation reaction equilibrium constant was related to the degree of polymerisation by the equation: $K_e = \frac{0.187}{1 - 19243 e^{-0.3932 i}}$ in

the range $i = 26 - 100$. The PBT polycondensation equilibrium constant at high degrees of polymerisation is in line with literature data and thermodynamics.

Keywords: 1,4-butanediol solubility; equilibrium constant; Flory-Huggins theory; polybutylene terephthalate; polycondensation

Introduction

Polybutylene terephthalate (PBT) is a high-performance, high molecular weight engineering resin. It was introduced in 1970 and its production grew rapidly as it found utility in automotive, electrical and other engineering applications. PBT shares many markets with polyethylene terephthalate (PET). PBT's temperature resistance is somewhat lower than that of PET but PBT is significantly easier to process and its temperature resistance is sufficient for most applications. Part of PBT's processing ease is due to its relatively low melt viscosity,

which makes it easier to transfer to moulds or extrusion dies. Moreover, its faster crystallization time allows for shorter closed mould times. Both of these properties contribute to shorter moulding cycles and account for much of PBT's increasing use in injection moulding.

PBT, like many industrially important engineering thermoplastic polymers is produced by a multistage polycondensation process carried out either batch wise or in a continuous manner. In the PBT polycondensation process, first the PBT prepolymer is produced by transesterification of dimethyl terephthalate (DMT) with 1, 4 – butanediol (BDO) or by esterification of terephthalic acid (PTA) with BDO. The PBT prepolymer produced during the esterification stage is further polycondensed in a second stage by a transesterification reaction, under continuous removal of BDO to obtain high molecular weight PBT.

The second stage is the transesterification reaction between PBT prepolymers. Transesterification is carried out between 240 and 260 °C. As the transesterification reaction goes to higher conversions the molecular weight of PBT increases and the viscosity of the reacting melt rises. The transesterification reaction (also referred to as polycondensation reaction) is strongly equilibrium limited. This means that removal of product BDO is an important aspect in industrial PBT polycondensation reactors. Removal of product BDO shifts the equilibrium towards the product side of the polycondensation reaction, thus assisting in achieving higher conversions. However since the viscosity of the PBT melt rises to as high as 1500 Pa.s, removal of BDO is difficult to achieve. Polycondensation equilibrium plays a vital role in the final stage of the PBT production, and is needed in the design of (new) reactors. In the present study the polycondensation equilibrium constant for PBT has been estimated.

Reaction and Equilibria

When starting from PTA, the first step in the production of PBT is the esterification reaction, in which one acid end group of PTA reacts with the one-hydroxyl end group (OH) of BDO, forming a carboxyl end group (EC) and hydroxyl end group (EOH). The carboxyl and hydroxyl end groups undergo further reactions leading to the formation of the prepolymer.

The esterification reaction is usually performed in one or more agitated reactors in series between 200 – 250 °C at pressures below 1 bar. When there is no more water being released from the reaction mixture, esterification is assumed to be complete. At the end of the esterification stage the reaction mixture primarily consists of hydroxyl end groups, repeating diester units and some carboxyl end groups. If the esterification stage is near completion (i.e. the amount of carboxyl end groups is negligible) the general structure of the PBT prepolymer produced from the esterification reaction is as shown in Figure 1. The prepolymer with an average degree of polymerisation i consists of two hydroxyl end groups and $i-1$ repeating diester units. The product of the esterification reaction is a prepolymer with i typically ranging from 1 to 10. The final product of the polycondensation reaction does have a degree of polymerisation around 100. The prepolymers formed by the esterification reaction are further polymerised by the aid of the polycondensation reaction to yield high molecular weight PBT.

Figure 1. General structure of PBT (pre) polymer having a degree of polymerisation of i .

In the polycondensation reaction, the hydroxyl end groups of the (pre) polymers undergo a transesterification reaction with increment in the chain length and release of BDO. To

accelerate the polycondensation reaction, a metal catalyst such as antimony, germanium, titanium or tin is used. The polycondensation reaction can be expressed by:

Based on the stoichiometry of the polycondensation reaction (Eq. [1]) and similarity with the definition of the equilibrium constant of the PET polycondensation reaction ^[1], the equilibrium constant (K_e) of the PBT polycondensation reaction can be defined in terms of the concentration of the repeating diester units ($[Z]$), hydroxyl end group of PBT ($[EOH]$) and $[BDO]$ concentration present in the reaction melt as:

$$K_e = \frac{[Z][BDO]}{[EOH]^2} \quad [2]$$

In addition to the esterification and polycondensation reactions, side reactions responsible for the degradation of hydroxyl end groups and BDO do also occur. These reactions lead to the formation of tetrahydrofuran (THF). The degradation reactions accompanying the esterification and polycondensation reaction can be represented by:

Polycondensation equilibrium studies of polyesters like PBT and PET are few in open literature. The polycondensation equilibrium of PBT and PET has been studied using model molecules ^{[2], [3] and [4]} and using PET prepolymer ^{[1], [5] and [6]}. Because of the lack of open literature data on the PBT equilibrium, the similarity of the polycondensation reaction of PET and PBT makes it worthwhile to use the PET polycondensation reaction as a reference. The main problem in studying the equilibrium both in PET and PBT system is the prevalence of side reactions (Eq. [3] and [4]) and esterification reactions during the later polycondensation stage of the polyester production.

Experimental

Experimental Set-up

The experimental determination of the polycondensation equilibrium constant was carried out in a batch reactor set-up (Figure 2). The set-up consists of a 2.36 litre steel batch reactor having an inner diameter of 112 mm and a height of 240 mm. The reactor was equipped with looking glasses. The reactor was mounted on a stand and could be tightly enclosed in a well conducting steel electric oven equipped with cartridge heaters. Thermocouples were present on the inner surface of the electric oven and the inside of the reactor. By varying the power supply to the cartridge heaters the temperature on the inner surface of the oven that was in contact with the reactor and thereby the temperature inside the reactor could be controlled. An anchor type stirrer (90 mm diameter and a length of 103 mm) was used in the batch reactor to stir the PBT melt. The reactor was connected to a water-cooled condenser via a heated polycondensation line. The condenser was further connected to the vacuum pump through a liquid nitrogen cooled vacuum trap. The vacuum pump was capable of maintaining a minimum pressure of 0.5 mbar in the reactor. A small valve just before the vacuum pump was used to maintain the pressure in the reactor at a specified pressure level.

Figure 2. Experimental set-up for the determination of the polycondensation equilibrium constant.

Materials and analysis method

The starting material used for the PBT polycondensation experiments was PBT prepolymer obtained from DSM Research, Geleen, The Netherlands. Chemical analysis and relative viscosity determination of the prepolymer was carried out at the department of performance materials – chemistry and technology of DSM research. The PBT prepolymer had a carboxyl end group concentration of $0.096 \text{ mole kg}_{\text{melt}}^{-1}$, hydroxyl end group concentration of $0.684 \text{ mole kg}_{\text{melt}}^{-1}$ and a melting point of 200°C . The combined weight percentage of BDO, water and THF in PBT prepolymer was less than 1 %. The initial degree of polymerisation of the PBT prepolymer was $i = 12.7$ with a repeating diester unit concentration of $4.06 \text{ mole kg}_{\text{melt}}^{-1}$. Dilute Solution Viscometry (DSV) was used to determine the relative viscosity of PBT samples produced in the batch reactor. In this DSV method, SCHOTT Ubbelohde capillaries of type 2 were immersed in a water bath maintained at 25°C . As it is not possible to determine the viscosity of the PBT melt at ambient conditions (since PBT solidifies) the

relative viscosity of a 1-weight % PBT solution in *m* – cresol was determined instead. A calibration curve from DSM, the Netherlands, was used to relate the relative viscosity of the solution of 1 weight % PBT sample in *m* – cresol to the average degree of polymerisation of the original sample¹.

Experimental procedure

Before starting the experiments the PBT prepolymer was crushed to obtain a fine powder. The batch reactor was thereafter filled with this powdered PBT prepolymer. The electric oven was fitted tightly around the batch reactor and was then heated so that the temperature inside the reactor reached a temperature around 255 °C. Initially the stirrer frequency was kept at 10 to 20 rpm. When the temperature inside the reactor reached 200 °C the prepolymer melted. Once the PBT prepolymer had melted, the vacuum pump was started. Vacuum in the range of 1 to 50 mbar was applied for various experiments. As vacuum was applied the gases generated in the PBT melt started evaporating and were condensed in the condenser with cooling water. With the application of vacuum and removal of BDO the polycondensation reaction inside the batch reactor can proceed (Eq. [1]). The rotation frequency of the stirrer was increased to a value of 300 rpm after the PBT prepolymer had melted. During the polycondensation reaction the concentration of repeating diester units increases and the concentration of hydroxyl end groups decreases. As the degree of polymerisation of PBT increases the viscosity and torque on the rotating shaft increase. At high viscosities of the PBT melt, the rotation frequency of the stirrer was reduced to maintain the torque on the rotating shaft below 3 Nm. After sufficiently long reaction times, the BDO concentration in the melt comes to equilibrium with the pressure maintained in the reactor. PBT samples could be withdrawn from the batch reactor by applying nitrogen over – pressure in the reactor. The heated valve attached below the reactor was kept at 255 °C to maintain PBT samples in melt form, as they were being withdrawn. The samples solidified immediately in the collecting vessel.

¹ The calibration curve cannot be given in this study because it involves proprietary knowledge of DSM, The Netherlands.

Results and Discussions

Equilibrium degree of polymerisation

In order to test the prevalence of equilibrium in the current experiments, various validation experiments at 255 °C were carried out. Along with the polycondensation reaction, the degradation reactions releasing THF (Eq. [3] and [4]) and the esterification reactions between carboxyl and hydroxyl end groups releasing water might also occur during the experiments. For a typical experiment performed at 255 °C and a pressure of 5 mbar, samples were withdrawn from the reactor at 95, 125 and 155 minutes after the experiment was started. Starting from an initial degree of polymerisation of 12.7 the degree of polymerisation of PBT during the 5 mbar polycondensation experiment rose to a value of 29.5 in 95 minutes. The degree of polymerisation remained constant at a value of 29.5 for the next successive samples taken at 125 and 155 minutes, within the range of the experimental error of 1 % in the determination of the relative viscosity. This constancy in the degree of polymerisation indicates that 1) equilibrium was attained; 2) the degradation reactions responsible for depolymerisation do not have a substantial influence on the experiments for the given experimental conditions. In order to determine the equilibrium constant of the PBT polycondensation reaction, equilibrium experiments were performed at various pressures ranging from 1 to 50 mbar. Polycondensation was typically carried out for about 130 minutes to be sure that equilibrium was attained. The degree of polymerisation achieved in the equilibrium experiments was determined using DSV with a 1 weight % solution of PBT in m – cresol. As the equilibrium pressure was varied from 50 to 1 mbar, for various experiments, the equilibrium relative viscosity increased from a value of 1.3 to 1.9. The increase in the relative viscosity is an indication of the increase in the degree of polymerisation with reduced equilibrium pressure. As the equilibrium pressure reduces the equilibrium BDO solubility in the PBT – BDO melt also reduces (Appendix 1), thereby enabling hydroxyl end groups to undergo the forward polycondensation reaction to a greater extent.

Figure 3. Experimentally determined equilibrium degree of polymerisation of PBT for polycondensation experiments performed in the range of 1 to 50 mbar BDO equilibrium pressure at 255 °C.

As the polycondensation reaction proceeds the concentration of repeating diester units increases and the degree of polymerisation rises. The variation of the degree of polymerisation with equilibrium pressure obtained experimentally at 255 °C is shown in Figure 3. The experimentally determined equilibrium degree of polymerisation (i) of PBT as a function of various equilibrium BDO pressures (P_{bdo}) can be best fitted with either of the following two expressions [5] and [6],

$$i = 111.47 - 86.18 \exp(-1.14 P_{bdo}^{-1.44}) \quad [5]$$

$$i = 105.06 - 81.42 \exp(-5.88 P_{bdo}^{-1.78}) \quad [6]$$

Once the equilibrium degree of polymerisation of PBT at various equilibrium pressures is known, the equilibrium repeating diester concentration and hydroxyl end group concentration can be determined using an overall mass balance from the degree of polymerisation as:

$$[Z] = \frac{(i-1) X_{pbt}}{(MW_Z(i-1) + 2 MW_{EOH})} \approx \frac{(i-1)}{(0.22i + 0.09)} \frac{\text{mole}}{\text{kg}_{\text{melt}}} \quad [7]$$

$$[EOH] = \frac{2X_{pbt}}{(MW_Z(i-1) + 2 MW_{EOH})} \approx \frac{2}{(0.22i + 0.09)} \frac{\text{mole}}{\text{kg}_{\text{melt}}} \quad [8]$$

Where $MW_Z = 0.22 \text{ kg mole}^{-1}$ is the molecular weight of a single repeating diester unit, $2MW_{EOH} = 0.31 \text{ kg mole}^{-1}$ is the molecular weight of a pair of hydroxyl end groups (attached to a single PBT molecule (see Figure 1)) and X_{pbt} is the mass fraction of PBT in PBT – BDO melt.

Dependence of equilibrium constant on the degree of polymerisation

The PBT polycondensation equilibrium constant expressed in terms of concentrations is given by equation [2]. Substituting the concentrations of Z (repeating diester unit from equation [7]), EOH (hydroxyl end groups from equation [8]) and BDO (equation [A1 - 1] of Appendix 1), in equation [2] gives the following expression for the equilibrium constant:

$$K_e = \frac{(i-1)(0.22i + 0.09)}{0.36} \frac{P_{bdo}}{P_{bdo}^S \exp \left[\chi + \left(1 - \frac{\hat{V}_{bdo}}{(i-1)\hat{V}_Z + 2\hat{V}_{eoh}} \right) \right] \left(\frac{0.22i + 0.09}{0.09} \frac{\hat{V}_{bdo}}{(i-1)\hat{V}_Z + 2\hat{V}_{eoh}} \right)} \quad [9]$$

The variation of the experimentally (smoothed) determined equilibrium constant with the degree of polymerisation is shown in Figure 4. The PBT polycondensation equilibrium constant as derived from equation [5] and [9] decreases from 0.86 to 0.2 as the PBT degree of polymerisation increases from 26 to 35 and above a PBT degree of polymerisation of 35 it attains a constant value of approximately 0.2.

Figure 4. Experimentally derived PBT polycondensation equilibrium constant as a function of the PBT degree of polymerisation at 255 °C. The PBT polycondensation equilibrium constant was determined using equation [9] and fitted experimental degree of polymerisation using: 1) Eq. [5] – $i = 111.47 - 86.18 \exp(-1.14 P_{bdo}^{-1.44})$ and 2) Eq. [6] – $i = 105.06 - 81.42 \exp(-5.88 P_{bdo}^{-1.78})$. The equilibrium constant in the range of $i = 26 - 100$ fitted the expression: $K_e = \frac{0.187}{1 - 19243 e^{-0.3932 i}}$ (equation [10]).

The PBT polycondensation equilibrium constant as derived from the fitted degree of polymerisation using equation [6] and [9] decreases from 0.9 to 0.28 as the PBT degree of polymerisation increases from 26 to 35 and increases from 0.28 to 0.5 as the PBT degree of polymerisation increases from 35 – 100. For PET Griehl et al. ^{[1], [7]} found that, the PET polycondensation equilibrium constant does not vary in the range of $i = 30 - 100$. Hence the PBT polycondensation equilibrium constant, using equation [5] and [9], which predicts a more or less constant equilibrium value of 0.2 in the range of $i = 35$ to 100, appears to be more consistent with previous work from literature for PET. In the range of $i = 26 - 100$ the PBT polycondensation equilibrium constant at 255 °C can therefore be given by equation [10] (see also Figure 4) as:

$$K_e = \frac{0.187}{1 - 19243 e^{-0.3932 i}} \quad [10]$$

The fact that in the range of $i = 26 - 35$ the polycondensation equilibrium constant increases as the degree of polymerisation decreases seems also logical from a fundamental point of view. The equilibrium constant can be defined in terms of the heat of reaction (ΔH) and standard entropy change (ΔS) and universal gas constant (R_g) as:

$$\ln K_e = \frac{-\Delta H}{R_g T} + \frac{\Delta S}{R_g} \quad [11]$$

Gupta et al.^[8] indicated that the equilibrium constant for the polycondensation of polyesters is independent of temperature (T). Hence from equation [11] it can be stated that the polycondensation equilibrium constant is mainly a function of the standard entropy change. If the degree of polymerisation of PBT increases, the number of PBT molecules per unit mass of the PBT melt decreases. Hence, with increasing degree of polymerisation the standard entropy change of the PBT melt decreases as the polycondensation reaction proceeds to higher conversions but becomes more or less constant at high degrees of polymerisation. Therefore it seems logical that the equilibrium constant decreases with increasing degree of polymerisation and stays constant at higher degrees of polymerisation.

Because of the similarity of the PET and PBT polycondensation reaction an evaluative comparison between the polycondensation equilibrium constants obtained experimentally using model molecules^{[2] and [3]} and using PET^[1], on one hand and the current PBT polycondensation equilibrium constant on the other, can be carried out. The various equilibrium constants are presented in Table 1. The experimentally observed ethanediol monobenzoate condensation equilibrium constant^{[2] and [3]} compares well with the PBT polycondensation equilibrium constant measured in the present study for degrees of polymerisation higher than 35. However the PET polycondensation equilibrium constant obtained by Challa^[1] slightly increases (from 0.12 to 0.26) with increasing degree of polymerisation, whereas in the present study it has been observed that the PBT polycondensation equilibrium constant decreases with an increasing degree of polymerisation (especially at low degrees of polymerisation). However, the reasoning in the previous section

shows that it seems logical that the equilibrium constant decreases with increasing degree of polymerisation as found in this study.

Table 1: Experimentally obtained equilibrium constants for PET and PBT polycondensation using model molecules and using PET (Challa^[1]) and PBT prepolymer (Present study).

*Experimentally derived, # Equilibrium constant derived from equation [10].

Authors	Reaction	Equilibrium Constant defined as per equation [2]
Reimschuessel et al. ^[2]	Ethandiol monobenzoate condensation	0.2 (202 °C), 0.19 (215 °C) 0.16 (226 °C)
Hovenkamp ^[3]	Ethandiol monobenzoate condensation	0.2 (197 °C)
Challa ^[1]	PET polycondensation	0.12 (254 °C and $i = 1.73$) 0.18 (254 °C and $i = 3.03$) 0.21 (262 °C and $i = 3.73$) 0.26 (262 °C and $i = 6.25$)
Present study	PBT polycondensation	0.86 to 0.2 (255 °C and $i = 26$ to 35)* ~ 0.2 (255 °C and $i = 35$ to 45)* 0.187 (255 °C and $i = 45$ to 100) [#]

Conclusions

The PBT polycondensation equilibrium constant has been determined at 255 °C using a batch reactor set-up. The experimentally determined PBT degree of polymerisation at various equilibrium pressures was used to obtain the value of the of PBT polycondensation equilibrium constant. The value of the PBT polycondensation equilibrium constant as a function of the PBT degree of polymerisation at 255 °C in the range of degree of polymerisation of 26 to 100 can be given by the following equation:

$$K_e = \frac{0.187}{1 - 19243 e^{-0.3932 i}} \quad [12]$$

The variation of the PBT polycondensation equilibrium constant with the PBT degree of polymerisation can be explained well using theoretical considerations, thermodynamics and literature data.

Appendix 1

The equilibrium BDO concentration can be derived as a function of equilibrium BDO pressure, and the degree of polymerisation of PBT based on the Flory Huggins theory, that can describe the behaviour of amorphous polymer – solvent systems^[9] as:

$$[BDO] = \frac{P_{bdo}}{P_{bdo}^s \exp \left[\chi + \left(1 - \frac{\hat{V}_{bdo}}{(i-1)\hat{V}_z + 2\hat{V}_{eoh}} \right) \right] MW_{bdo} \left(\frac{0.22 i + 0.09}{0.09} \frac{\hat{V}_{bdo}}{(i-1)\hat{V}_z + 2\hat{V}_{eoh}} \right)} \quad [A1-1]$$

$\hat{V}_{bdo}$, $\hat{V}_z$ and $\hat{V}_{eoh}$ are the molar volumes of BDO, Z and EOH respectively. The molar volumes of repeating diester units, hydroxyl end groups and BDO have been calculated based on the group contribution method of Sugden and Biltz^{[10], [11]}. The dependence of the molar volumes of Z, EOH and BDO on temperature are assumed to be identical^[12] which basically means that the effect of temperature cancels out when the ratio of molar volumes of Z, EOH and BDO are taken. Hence in the equations where the terms corresponding to repeating diester units, hydroxyl end groups and BDO molar volumes appear, molar volumes at 0 K have been taken. The molar volumes of the repeating diester units, BDO and two hydroxyl end groups at absolute zero have been determined as $2.1413 \cdot 10^{-4}$, $1.0503 \cdot 10^{-4}$ and $3.1916 \cdot 10^{-4} \text{ m}^3 \text{ mole}^{-1}$, respectively^{[10] and [11]}. The value of the Flory Huggins interaction parameter χ is in the range $0.3 - 0.5$ ^[10] for amorphous polymers – solvent systems. The DSM UNIFAC – FV model was used to determine the value of the parameter χ for the PBT – BDO system.²

² The exact value of the interaction parameter cannot be given in this study because it involves proprietary knowledge of DSM, the Netherlands.

Acknowledgements

The authors wish to thank Henk Jan Moed of the research group OOIP, University of Twente, for building the batch reactor set-up and helping out in solving the operational problems. The authors also wish to thank Panagiotis Pagonas and Mark Verkerk for their contribution in the experimental work and Dr. Paul van den Heuvel of DSM Research, Geleen, for carrying out the carboxyl and hydroxyl end group analysis of the PBT samples.

- [1] G. Challa, PhD Thesis, University of Amsterdam 1959.
- [2] H.K. Reimschuessel, B.T. Debona, A.K.S. Murthy, *J. Polym. Sci. Polymer Chemistry Edn* **1979**, 17, 3217.
- [3] S.G. Hovenkamp, *J. Polym. Sci: Part A –I* **1971**, 9, 3617.
- [4] R. Pilati, P. Manaresi, B. Fortunato, A. Munari, V. Passalacqua, *Polymer* **1981**, 22, 799.
- [5] K. Tomita, *Polymer* **1973**, 14, 50.
- [6] H. Yokoyama, T. Sano, T. Chijiwa, R. Kajiya, *J. Japan Petrol. Inst.* **1978**, 21(1), 58.
- [7] W. Griehl, P.F. Förster, "*Faserforsch. u. Textiltechn.*" **1956**, 7, 463.
- [8] S.K. Gupta, A. Kumar, Plenum Press, New York 1987.
- [9] J.S. Vrentas, J.L. Duda, S.T. Hsieh, *I & EC, Prod, Dev, Res* **1983**, 22, 326.
- [10] S. Sugden, *J. Chem. Soc.* **1921**, 1786.
- [11] W. Biltz, "*Rauchemie der Festen Stoffe*" **1934**, Voss, Leipzig.
- [12] K.D. Samant, K.M. Ng, *AIChE J.* **1999**, 45, 8.