Comparison Between Titanium Tetrabutoxide and a New Commercial Titanium Dioxide Based Catalyst Used for the Synthesis of Poly(Ethylene Terephthalate)

Lara Finelli,[1] Cesare Lorenzetti,[2] Massimo Messori,[3] Laura Sisti,[1] Micaela Vannini[1]

[1]*Dipartimento di Chimica Applicata e Scienza dei Materiali, Viale Risorgimento 2, Bologna, Italy*
[2]*Dipartimento di Discipline Economico Aziendali, Area Tecnologia e Valorizzazione delle Risorse, Piazza Scaravilli 2, Bologna, Italy*
[3]*Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Via Vignolese 905, Modena, Italy*

ABSTRACT: Titanium-based catalysts for poly(alkylene terephthalate) synthesis have been known for many years. Up to now, organotitanate compounds are used as catalysts on an industrial scale only for the synthesis of poly(butylene terephthalate) (PBT), poly(trimethylene terephthalate) (PTT), and related copolyesters; for poly(ethylene terephthalate) (PET), synthesis antimony-based catalysts are preferred. In fact, in this case, titanium is known to cause undesirable discoloration. In this article, a study of PET synthesis using different concentrations of a new titanium dioxide based catalyst (C-94), commercially available from Acordis Industrial Fibers GmbH, is carried out and compared with the results obtained with titanium tetrabutoxide (TBT) catalyst in the same experimental conditions. The solid-state properties and composition of C-94 was investigated by thermogravimetric analysis (TGA) coupled with mass spectroscopy and by X-ray powder diffraction (XRD). A characterization of the polymers prepared with C-94 and TBT is also described. The results have shown that the use of C-94 leads to more hydrolytically stable polymers, whereas no evidence of difference in the catalytic activity, carboxyl end-groups concentration, diethylene glycol content, and thermal properties were revealed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1887–1892, 2004

Key words: polyesters; synthesis; catalysts; structure–properties relations

INTRODUCTION

Several catalytic systems are known for terephthalate polyesters synthesis but, up to now, only titanium- and antimony-based catalysts are used on an industrial scale because of their ability to combine the economic and the performance requirements for industrial productions.

Titanium-based catalysts have been known for many years and actually are used for poly(butylene terephthalate) (PBT) and poly(trimethylene terephthalate) (PTT) production,[1,2] whereas antimony-based catalysts are commonly used for poly(ethylene terephthalate) (PET) synthesis.[3] These latter are preferred because they prevent polymer yellow discoloration that is always occurring when titanium-based catalysts are used during the polycondensation stage of PET synthesis. In fact, this stage is conducted at a higher temperature than the one used for the other two polyesters, due to the higher melting temperature of PET. In addition, titanium alcoxides were reported to influence negatively the hydrolytic stability of poly-

esters; in fact, they promote degradation reactions that lead to the formation of carboxylic end groups, which are responsible for the poor thermal and hydrolytic stability of polyesters.[4,5]

The discoloration, occurring when titanium alkoxides are employed, is usually attributed to organic contaminants formed during the polymerization process, whereas for antimony catalysts, gray discoloration is mainly due to elemental metal formed by a mechanism proposed by Aharoni.[6,7]

At the moment, the use of antimony compounds, in particular, antimony trioxide and antimony glicoxides, constitutes a problem, especially when PET is used for food packaging or for drinking water and soft-drink bottles. Moreover, glycol residues, derived from PET production, contain antimony, and for this reason, either have to be disposed of as hazardous waste or must be burnt in special ovens. In addition, a considerable amount of antimony compounds may be released, from the materials, representing an important health risk. Although at present studies on the toxicity for humans are not enough, some indications that antimony trioxide could interfere with embryonic and fetal development exist. The International Agency for Research on Cancer (IARC) considered antimony trioxide as possibly carcinogenic for man.[8] Therefore,

a very important task for polyester catalysis is represented by the preparation of new antimony-free catalysts with low environmental impact.

Germanium is an excellent catalyst for PET and leads to polymers with a unique set of properties in terms of whiteness, molecular weight, and hydrolytic stability. Unfortunately, it is not largely used because of its prohibitive price, due to its highly restricted availability; at present, only a small percentage of the total worldwide production of PET makes use of germanium compounds. Germanium is not a real alternative for antimony-based catalysts, which, since the 1970s, are almost exclusively used, essentially for economic reasons.[9] For the reasons mentioned above, PET manufacturers are now focusing on potential alternatives to antimony compounds able to offer a good compromise among food contact regulations, activity, cost, and color. At the moment, the only alternative to antimony-based catalyst that meets the above criteria is titanium.

Several companies are now developing titanium-based catalyst systems; among them Tioxide Specialties,[10] DuPont[11–14] Zimmer and Sachtleben,[15] Akzo Nobel,[16] Atochem[17] and Hoechst[18] have patented in this area. These latest catalysts are designed to be stable and have been formulated to give a balance of good activity and good color. In this article, we present a comparison between the first generation of a titanium catalyst, titanium tetrabutoxide (TBT), and a new titanium dioxide based catalyst, C-94, that was supplied from Acordis Industrial Fibers GmbH and characterized by thermal gravimetric analysis (TGA) coupled with mass spectroscopy and by X-ray diffraction (XRD) analysis. The screening of the catalytic activity of these systems was performed on the polymerization of PET by using different amounts of these two catalysts. The polymers prepared were also characterized; in particular, the carboxylic end-groups content, the thermal properties, and the diethylene glycol (DEG) content were measured. The DEG level in PET is a key parameter; in fact, DEG is a naturally occurring byproduct of PET manufacture and, depending upon the polymerization route, the amount of DEG in the final polymer will vary.[19]

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) and ethylene glycol (EG), from Aldrich, were high-purity reagents and were not purified before use. TBT (Aldrich) was distilled under vacuum before use. Commercial C-94 was a gift from Acordis Industrial Fibers GmbH (Wuppertal, Germany).

PET synthesis

PET was synthesized starting from DMT (70.0 g; 0.360 mol) and EG (49.2 g; 0.793 mol) (EG/DMT = 2.2M

ratio), with TBT and C-94 as catalysts. In particular, 24.6 and 49.2 mg of TBT and 7.7 and 15.4 mg of C-94 were used. These amounts correspond to 50 and 100 ppm of titanium and are calculated on the basis of the polymer theoretical yield, the technical data of Acordis,[20] and our TGA characterization results on the catalyst. Precisely, the titanium content used to represent C-94 is 74.7 wt %.

The syntheses were carried out according to the usual two-stage polycondensation procedure in a 250-mL round-bottom wide-neck reactor, closed at the top with a three-neck flat flange lid equipped with a mechanical stirrer (driven at 50 rpm) and a torque meter to monitor the viscosity of the reaction melt during the polymerization. The lid was heated at a temperature of 90°C with a heating band and two graduated condensers in a series (the first was water cooled and the second was liquid nitrogen cooled) were connected to the reactor to collect volatile products during the first and second stage. The reactor was heated by a thermostated oil bath in which the system was placed. In the first stage, conducted at atmospheric pressure, the temperature of the oil bath was kept at 210°C, after 10 min at 160°C, and maintained there until 95% of the theoretical amount of methanol, that was continuously measured, was distilled off. In the second stage, the pressure was slowly reduced from atmospheric down to 1–0.5 mbar and the temperature was raised up to 280°C until the end of the run. Moreover, to evaluate the polymerization evolution, the reaction mixture was sampled after 75 and 135 min from the beginning of the second stage, which means when the vacuum was applied.

Catalyst characterization

TGA measurement was performed with a TA Instruments TGA2950 thermogravimetric analyzer (purge gas = helium, scan rate = 10°C/min). The released volatile products were directly transferred to a quadruple mass spectrometer (Balzers Thermo-Star GSD 300T; temperature setting of the interface = 200°C, mass range = 10–300 amu, CH-tron detector = 1400 V).

XRD analysis was carried out at room temperature with a Bragg/Brentano diffractometer (Philips PW 1050/61-PW1710) equipped with a graphite monochromator in the diffracted beam, using Cu anode as X-ray source. A flat sample holder, 1.5 mm deep, was filled with synthesized PSDEA powder. Data were collected in the 2θ range of 2.2–80°, counting for 10 s at each 0.03° step.

Polymer characterization

Carboxyl end-group content was determined by potentiometric titration by using a DL 25 automated
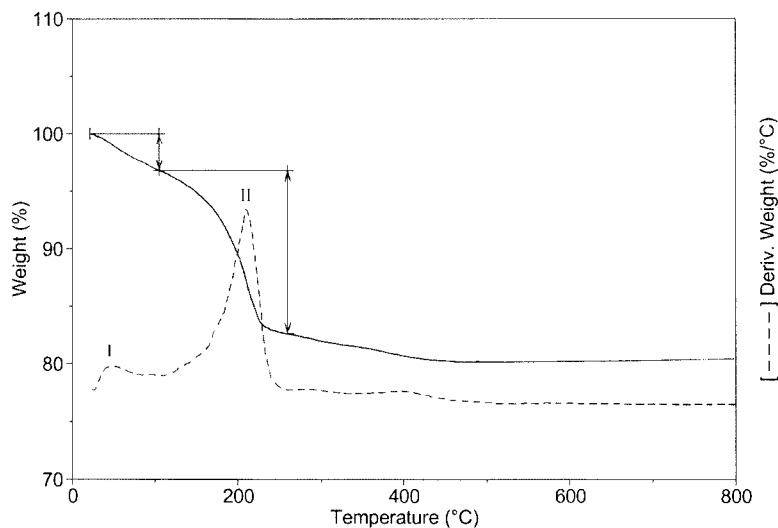
Figure 1   Thermogravimetric curve of C-94.

titration system equipped with an SC-111 combination electrode from Mettler. About 0.5–1 g of polymer was dissolved in about 20 mL hot o-cresol/methylene chloride (75/25 v/v) solution. Once dissolved, the solution was allowed to cool to room temperature and then about 50 mL methylene chloride was added. The solution was titrated with $0.01N$ tetrabutyl ammonium hydroxide and the carboxyl concentration was expressed in milliequivalents per kilogram (meq/kg). The standard deviation of the measurements is lower than 0.85 meq/kg.

The differential scanning calorimetric (DSC) measurements were carried out by means of a Perkin–Elmer DSC7 instrument equipped with a liquid sub-ambient accessory and calibrated with high-purity standards (indium and cyclohexane). The external block temperature control was set at $-60°C$. With the aim of measuring the glass transition and the melting temperatures of the polymers under investigation, weighed samples (ca. 10 mg) were encapsulated in aluminum pans and heated up to 280°C at a rate of 20°C/min (first scan), kept at this temperature for 3 min, and then rapidly quenched to $-10°C$. Finally, they were reheated from $-10°C$ up to 280°C at a heating rate of 20°C/min (second scan). The glass-transition temperature (T_g) was taken as the midpoint of the heat capacity increment (Δc_p) associated with the glass-to-rubber transition. The melting temperature (T_m) and the crystallization temperature (T_c) were determined as the peak value of the endothermal and exothermal phenomenon in the DSC curve, respectively. The specific heat increment Δc_p, associated with the glass transition of the amorphous phase, was calculated from the vertical distance between the two extrapolated baselines at the glass transition temperature. The heat of fusion and the heat of crystallization of the crystal phase were calculated from the area of

the DSC endotherm and exotherm, respectively. Repeated measurements on each sample showed excellent reproducibility. To determine the crystallization rate under nonisothermal conditions, the samples were heated to 30°C above fusion temperature at 20°C/min, kept there for 1 min, and then cooled at 10°C/min. The temperature corresponding to the maximum of the exothermic peak in the DSC cooling curve (T_{cc}) was taken as indicative of the crystallization rate.

Thermogravimetric curves were obtained both in air and under nitrogen atmosphere by using a Perkin–Elmer TGA7 apparatus (gas flow: 50 mL/min) at 10°C/min heating rate up to 900°C.

Gel permeation chromatography (GPC) measurements were performed on a HP 1100 Series equipped with a PL gel 5 μ Mixed-C column and a UV detector set at 254 nm. A mixture of chloroform/methylene chloride/1,1,1,3,3,3-hexafluoro-2-propanol (75/20/5 wt/wt) was used as eluant. The injected solution had a sample concentration lower than 0.1 wt %. The molecular weights were determined by using a calibration curve obtained from polystyrene standards.

^{1}H-NMR spectra were recorded on a Varian XL-300 spectrometer (chemical shifts are downfield from tetramethylsilane). The solvent used was deuterated chloroform or a mixture of deuterated trifluoroacetic acid/deuterated chloroform (20/80 wt/wt) depending on the sample analyzed.

Hydrolytic stability of polymer samples was determined by immerging a set of vials containing powder of the polymers, in boiling water and removing samples with time. The degree of hydrolytic degradation was monitored by measuring the carboxyl end-groups content of the polymer, because each hydrolysis event results in the generation of a carboxyl end group.
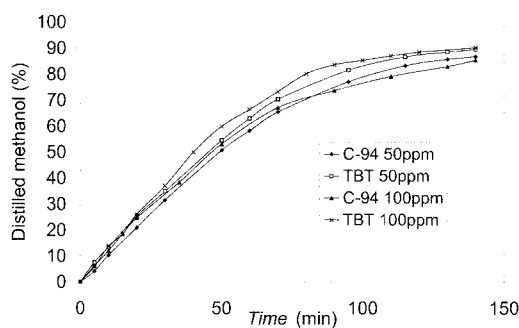
Figure 2 PET first-stage synthesis: comparison of the distilled methanol versus reaction time using TBT and C-94 as catalysts.

Figure 3 M_n increase during PET second-stage synthesis.

RESULTS AND DISCUSSION

The solid-state properties of C-94 were investigated by means of TGA coupled with mass spectroscopy and by XRD, which revealed that the catalyst at room temperature is completely amorphous; in fact, its XRD profile did not present any reflections.

Figure 1 shows the TGA curve of C-94. The catalyst thermal degradation occurs above 150°C and is composed of a first step (I), where about 3% of the initial weight is lost, followed by a second step (II), where the loss is 14%. The two degradation events are centered at 49 and 209°C, respectively. Eighty-three percent of the solid residue remains above 250°C. The mass spectra collected during the TGA measurement show the presence of water in the first degradation step (I), from room temperature to about 105°C. In the latter degradation step (II), from 105 to 260°C, the propanoxide and ethanoxide fragments, arising from the reagents used to prepare the catalyst, are observed.[21]

To evaluate and compare the catalytic activity of TBT and C-94, a study of the reaction evolution between DMT and EG for PET synthesis using several amount of the catalysts was carried out. In particular, two different concentrations of the catalysts were employed, 50 and 100 ppm, calculated as elemental titanium on the basis of the polymer theoretical yield, the technical data of Acordis, and the catalyst TGA characterization. The syntheses and the final polymers obtained are called C-94 50 ppm, C-94 100 ppm, TBT 50 ppm, and TBT 100 ppm, depending on the amount and type of catalyst used during the polymerization. The first-stage synthesis was investigated by measuring the amount of volatile byproduct (methanol) collected in a water-cooled condenser. In Figure 2, the distillation curves obtained are presented. From this chart, it is possible to deduce that there is no difference in the activity of the two catalysts during the first reaction stage.

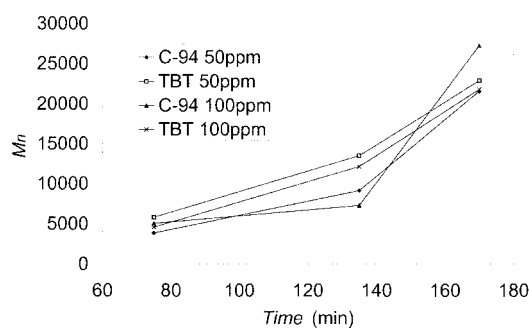The molecular weight increase during the second stage (Fig. 3), measured by GPC, was used as an indication of the second-stage evolution; the initial time was taken when vacuum was applied. Again, also in this case, it comes out that no difference is arising by the use of the two catalytic systems. Moreover, the final polymer colors seemed not to differ by each other, even if during the polymerization the reaction melt with C-94 showed greater clarity.

The final molecular weight is reported in Table I together with the carboxyl end groups and DEG content, determined by titration and ^{1}H-NMR analysis [δ = 4.15 ppm (bm, 4H)], respectively. Their level on PET depends on experimental conditions, particularly temperature, reaction time, and type of catalyst.[22]

As can be seen, the polymers synthesized do not significantly differ from each other. For this reason, we have decided to carry out hydrolytic stability tests; in fact, as mentioned in the Introduction, titanium alkoxide catalysts were reported to play a role in the polyesters carboxyl end-groups formation. The chart in Figure 4 reports the carboxyl groups content versus time of degradation in boiling water. What is remarkable is the difference in the increment between the polymer sampled after the second day of aging; in fact, in the case of TBT, this value is almost double, indicating a higher degradation activity using this catalyst.

The thermal behavior of PET samples was investigated by thermogravimetric analysis and differential scanning calorimetry. The investigation on the thermal stability was carried out both in air and under nitrogen atmosphere. In all cases, the weight loss takes place practically in one step, and the samples under investigation were found to be characterized by anal-

TABLE I
Characterization Results of PET Samples

Polymer	—COOH in meq/kg	DEG in mol %	M_n
TBT (50 ppm)	6.0	0.8	22,850
TBT (100 ppm)	5.2	1.8	21,756
C-94 (50 ppm)	4.1	1.1	21,530
C-94 (100 ppm)	7.3	1.5	27,756
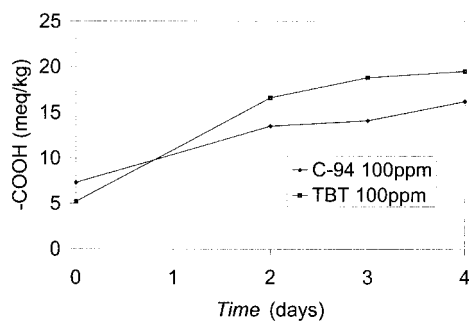
Figure 4 Carboxyl end-groups content of PET samples after hydrolytic degradation.

Figure 5 DSC crystallization exotherms of PET samples cooled from the melt at 10°C/min.

ogous thermal stabilities, being all practically stable up to 380°C.

As far as the calorimetric measurements are concerned, the data obtained are collected in Table II. As regards the calorimetric traces relative to the first scan, in all cases, a melting endotherm is present: peak location and the heat of fusion are similar for all samples, indicating that no appreciable difference on the melting phenomenon was found in the samples under investigation.

To study the glass transition phenomenon, the samples were quenched from the melt (see second-scan data): all the quenched samples are characterized by a glass transition followed by an exothermal cold crystallization peak and a melting endotherm at higher temperature. Table II shows that the enthalpy of crystallization compares very well with the corresponding heat of fusion, indicating that the polymers are completely amorphous after melt quenching.

The experimentally measured T_g, T_c, and T_m appear to be very similar for all samples and in agreement with the data reported in the literature.[23] No significant change in the glass transition phenomenon was found for PET samples.

To get results on the effect of the type and amount of catalyst, molecular weight, carboxyl end groups, and DEG content on the crystallization rate of PET samples, nonisothermal experiments were carried out, subjecting the samples to the thermal treatment described in Experimental. It is worth remembering that the half-time of primary crystallization in isothermal
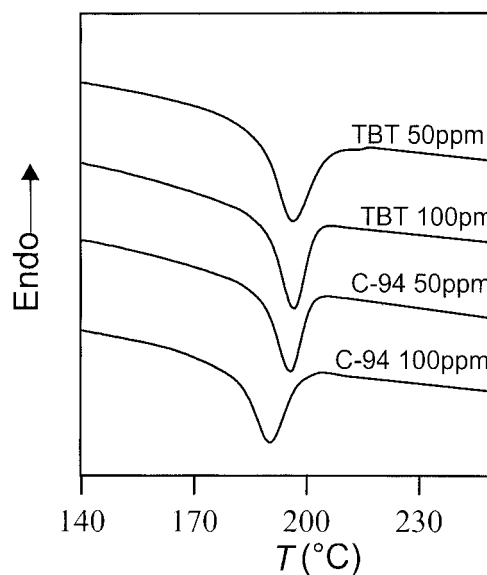
experiments correlates with the temperature corresponding to the maximum of the crystallization peaks in nonisothermal experiments[24] (T_{cc}), being this latter is more easily obtainable. The exothermic crystallization peaks of the samples under investigation are reported in Figure 5 and the corresponding data are reported in Table II. It can be observed that the temperatures corresponding to the maximum of the exothermal crystallization peak are similar, except for the C-94 100 ppm polymer, which has a lower T_{cc} value. This behavior can be explained taking into account that this sample has the higher content of —COOH end groups and the higher molecular weight, determining a decrease in the chain mobility, and therefore, a decrement in the crystallization rate.[25,26]

Further investigations on the crystallization rate in nonisothermal conditions of PET samples are in progress.

CONCLUSION

In conclusion, TBT and the new titanium dioxide based catalyst C-94 for PET synthesis showed compa-

TABLE II
Thermal Characterization Data of PET Samples

	1st scan				2nd scan				
Polymer	T_m (°C)	ΔH_m (J/g)	T_g (°C)	ΔC_p (J/g°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)
TBT (50 ppm)	250	57	82	0.358	160	37	249	39	197
TBT (100 ppm)	251	59	81	0.362	159	38	250	41	197
C-94 (50 ppm)	253	61	80	0.355	159	37	251	38	196
C-94 (100 ppm)	252	58	80	0.368	162	36	251	37	190

rable catalytic activity in our experimental setup. The C-94 composition analysis showed that this catalyst contains a significant amount of alkoxides that are probably responsible for the very similar concentration of the final carboxyl end groups and DEG, found in the polymers. Furthermore, the same behavior occurs for their thermal properties. The only important difference between the two catalysts was found in the hydrolytic stability of the polymers; in fact, C-94 seems to give rise to a smaller extent of degradation. In addition, considering the intrinsic higher hydrolytic stability of C-94 compared to TBT, this new catalyst provides a good alternative for polyesters production to titanium alkoxide and also to antimony-based catalysts. In fact, in respect to TBT, it offers a better polymer stability and catalyst handling and, respect to antimony-based catalysts, a higher catalytic activity and a lower environmental impact.

References

1. Traub, H. L.; Hirt, P.; Oppermann, W. Angew Makromol Chem 1995, 230, 179.
2. Pilati, F. in Comprehensive Polymer Science, 1st ed.; Allen, G.; Bevington, J. C., Eds., Pergamon Press: Oxford, 1989; Vol. 5, Chapter 17, p. 308.
3. Pilati, F. in Comprehensive Polymer Science, 1st ed.; Allen, G.; Bevington, J. C., Eds., Pergamon Press: Oxford, 1989; Vol. 5, Chapter 17, p. 306.
4. Pilati, F.; Munari, A.; Manaresi, P.; Bonora, V. Polymer 1985, 26, 1745.
5. Ravens, D. A. S.; Ward, I. M. Trans Faraday Soc 1967, 21, 557.
6. Aharoni, S. M. Int J Polym Mater 2001, 48, 425.
7. Aharoni, S. M. Polym Eng Sci 1998, 38, 1039.
8. Léonard, A.; Gerber, G. B. Mutat Res 1996, 366, 1.
9. MacDonald, W. A. Polym Int 2002, 51, 923.
10. Tioxide Specialties Ltd., U.S. Pat. 5,866,710, 1999.
11. DuPont, U.S. Pat. 6,166,170, 2000.
12. DuPont, U.S. Pat. 6,080,834, 2000.
13. DuPont, U.S. Pat. 6,066,714, 2000.
14. DuPont, U.S. Pat. 6,034,203, 2000.
15. Zimmer Aktiengesellschaft, Sachtleben Chemie, EP Pat. 736,560, 1996.
16. Akzo Nobel, U.S. Pat. 5,789,528, 1998.
17. Elf Atochem North America, Inc., EP Pat. 970,983, 2000.
18. Hoechst Celanese Corp., U.S. Pat. 5,922,828, 1999.
19. Maréchal, E. in Handbook of Thermoplastic Polyesters, 1st ed.; Fakirov, S., Ed., Wiley-VCH: Weinheim, 2002; Vol. 1, Chapter 1, p. 28.
20. Thier Grebe, R.; Rabe, M. Melliand Intern 2000, 4, 298.
21. Akzo Nobel, U.S. Pat. 5,684,116, 1997.
22. Maréchal, E. in Handbook of Thermoplastic Polyesters, 1st ed.; Fakirov, S., Ed., Wiley-VCH: Weinheim, 2002; Vol. 1, Chapter 1, p. 29.
23. Karayannidis, G. P.; Sideridou, D. I.; Zamboulis, D. N.; Bikiaris, D. N.; Sakalis, A. J. J Appl Polym Sci 2000, 78, 200.
24. Legras, R.; Bailly, C.; Daumerie, M.; Dekoninck, J. M.; Mercier, M. P.; Zichy, V.; Nield, E. Polymer 1986, 27, 109.
25. Berti, C.; Bonora, V.; Colonna, M.; Lotti, N.; Sisti, L. Eur Polym Mater 2003, 39, 1595.
26. Gunther, B.; Zachmann, H. G. Polymer 1983, 24, 1008.