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Physical properties of poly(ester-urethanes) prepared from different molar mass polycaprolactone-diols

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Abstract

Segmented poly(ester-urethanes) (PEUs) based on poly(ϵ-caprolactone) (PCL) as a soft segment and a non-aromatic diisocyanate in the hard segment were synthesized. The soft segment crystallinity and other physical properties of the PEUs were studied. It was found that the crystallinity and rate of crystallization of the PCL continuous phase in the PEUs decreases and the glass transition temperature of PEUs increases in comparison with the PCL prepolymers. The restriction of the crystallization of the PCL soft segment depends on the hard segment concentration, length of the soft segment, and total molecular weight of the PEUs. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Segmented polyurethanes are composed of alternating soft (low glass transition) segments and more rigid, polar urethane (hard) segments. The soft segments are generally polyethers [1–13] or polyesters [1–3,12,14–22] and the hard segments are formed from the extension of a diisocyanate terminated prepolymer with a low molecular weight diol.

Depending on the soft segment or hard segment concentration the polymer has a continuous hard phase with a dispersed soft phase, a continuous soft phase with dispersed hard phase, or a bicontinuous phase [23–25]. The polyurethanes with a continuous soft phase exhibit elastomeric or thermoplastic behavior at room temperature depending on the molecular weight and crystallinity of the soft segment.

The existence of a microphase separation caused by clustering of the hard and soft segments into separate domains is well established [4,6–8,10,11,13,26–28].

We have recently been involved in a collaborative program [29] focusing on the synthesis and evaluation of non-toxic biodegradable polymers which could undergo environmental degradation. In our previous work it was shown that the degradation of PCL and its copolymers proceeds mainly enzymatically and depends on the chemical structure, molecular weght, composition and morphology of the polymers [30]. In the context of these results polyurethanes based on PCL and non-aromatic diisocyanate were synthesized and evaluated.

For this work 1,1′-methylene-bis(4-isocyanatocyclohexane) (hydrogenated diphenylmethane diisocyanate) (HMDI), a commercially available non-aromatic diisocyanate, was used.

The combination of HMDI as hard segment and PCL as soft segment in PEUs is limited and only a low molecular weight soft-segment (varying from 830 to 2000) is used [3,12,15]. The PEUs with an aliphatic hard segment (HMDI) have mostly amorphous hard segment domains [15].

Studies concerning the influence of PCL soft segment molecular weight and hard segment concentration on crystallizability and properties of PEUs based on an aromatic or aliphatic hard segment have been published previously [3,12,14,15,17,18,20]. Generally, when the length of the soft segment increases and the concentration of the hard segment decreases, the crystallizability of the polyurethanes increases [15,31].

Our preliminary data on the degradation of PEUs based on PCL in the presence of fungi and by composting showed that the length of the PCL segment and also the composition and morphology of PEUs play an important role on the biodegradability of the polymers [32].

The investigation of the physical properties of the PEUs with respect to their composition would be important in the

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further considerations about their enviromental degradation and proper application as degradable materials.

This work presents our recent results from synthesis and investigation of the morphology and properties of poly(ester-urethanes) based on poly-ϵ-caprolactone with different molecular weight ($M_W = 2000$, 4000 and 7300) as a soft segment and a non-aromatic diisocyanate (HMDI) extended with butanediol as a hard segment. The combination of HMDI as a hard segment and PLC soft segment with higher molecular weight ($M_W = 4000$ and 7300) is explored for the first time and allows us to study and compare the soft segment crystallinity and other physical properties of PEUs with respect to the PCL length and hard segment concentration.

2. Experimental

2.1. Materials

ϵ-Caprolactone and butanediol (Aldrich Chemical Co., Milwaukee, WI) were distilled from calcium hydride prior to use. Poly(ϵ-caprolactone) diols with molecular weights of 2000 and 4000 were kind gifts from Solvay Co., Belgium. PCL diol with a molecular weight of 7300 was synthesized by ring opening polymerization of ϵ-caprolactone initiated with 1,6-hexanediol by the procedure described in the literature [33]. All PCL diols were dried over P_2O_5 under vacuum prior to use in the synthesis of PEUs. 1,1′-Methylene-bis(4-isocyanatocyclohexane) (Desmodur W, Bayer A.G.), stannous octoate (Sigma Chemical Co., St Louis, MO), methylene chloride, and hexane were used as received.

2.2. Procedure

The synthesis of poly(ester-urethanes) was performed in bulk under an argon blanket at 65°C. A typical experimental procedure was as follows: PCL diol (1 eq) was heated at 65°C during 30 min. 1,1′-methylene-bis(4-isocyanatocyclohexane) (2.1 eq) and two drops of stannous octoate were added to the melt. After stirring for 30 min at 65°C, butanediol (1 eq) was added and the reaction mixture was stirred for another 1 h. The polymers were isolated by dissolving the reaction mixture in methylene chloride, followed by precipitation in hexane.

2.3. Methods

Molecular weight and molecular weight distribution of the polymers were measured by gel permeation chromatography (GPC) using a mixed gel column (Polymer Laboratories), polystyrene standards, and chloroform as eluent.

^1H NMR spectra were recorded on a Bruker 360 MHz spectrometer in $CDCl_3$, at room temperature with tetramethylsilane as the internal standard. The hydroxyl functionality of the prepolymers was determined using ^1H NMR analysis of the reaction products between diol-terminated polymers and trichloroacetylisocyanate (TAIC) [34].

Wide angle X-ray diffraction measurements (WAXS) were carried out with a Philips PW1050/81 diffractometer controlled by a PW1710 unit, using a graphite monochromatized Cu K_α radiation ($\lambda = 0.1542$ nm; 40 kV; 40 mA). The percentage of crystallinity was calculated through graphical integration of the diffracted intensity data in the 2θ range 10–60° and subtraction of the amorphous scattering band intensity.

Three different instruments were used for DSC measurements: (1) DSC 2920, TA instruments, in the normal mode for melting and crystallization transition and in modulate mode (oscillation amplitude 0.5°C, oscillation period 40 s) for glass transition; (2) DuPont 9900 for measurements on melt quenched samples; and (3) DSC-7, Perkin Elmer, for isothermal crystallization measurements.

The glass transition temperature (T_g) was taken at the midpoint ($1/2\Delta c_p$) of the stepwise increasing of the heat capacity. The heat capacity calibration was made by running a standard sapphire (Al_2O_3) sample. The cell constant was calibrated using a standard indium sample.

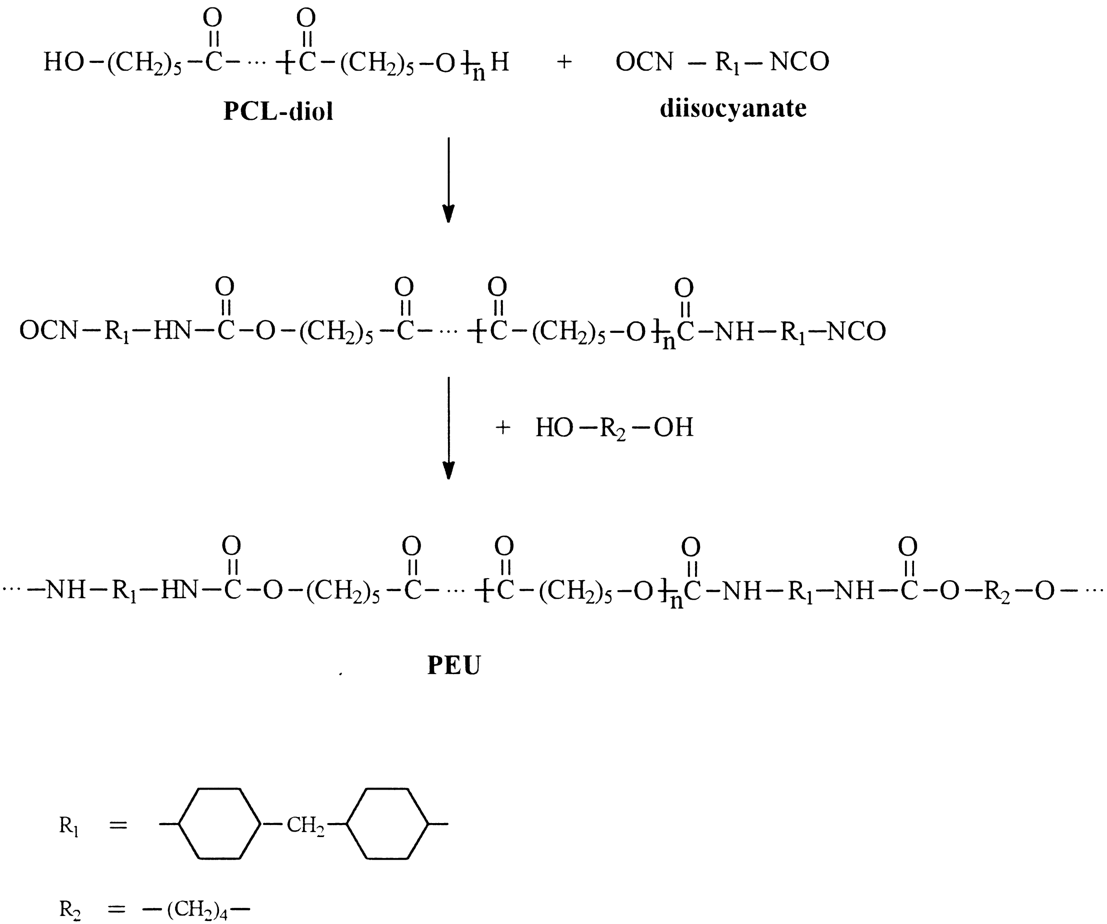
For isothermal experiments the following procedure was used: the samples were first melted at 80°C for 5 min and then rapidly (60°C min^{-1}) cooled to a selected crystallization temperature, T_c, and kept at this temperature to the end of the exothermic crystallization peak. The heat evolved during the isothermal crystallization was recorded as a function of time.

The melting temperature and the enthalpy of fusion of the samples after their isothermal crystallization were measured with the same equipment. The melting curves were recorded after heating of the samples from the crystallization temperature to a temperature above the melting point at a heating rate of 10°C min^{-1} without any previous cooling of the samples.

A BHSM Olympus polarizing microscope fitted with THMS 600 Linkam hot stage was used to observe the crystallization behavior of thin layers of PEUs solutions during the evaporation of the solvent at room temperature or thin films of PEUs with the same melting–crystallizing cycles as used in the DSC isothermal crystallization studies.

Dynamic mechanical measurements were performed with a DMTA, Polymer Laboratories Ltd, operated in the dual cantilever bending mode, at a frequency of 3 Hz and a heating rate of 3°C min^{-1} on samples in the form of injection molded bars ($30 \times 7.5 \times 1.5$ mm^3). DMTA measurements were carried out at least 8 weeks after injection molding in order to obtain equilibrium crystallinity.

It can be expected that the different procedures for sample preparation (precipitation, casting from solution and injection molding) lead to various structure formation and properties of PEUs. It is due to the different crystallization conditions for PEUs: crystallization from solvent–nonsolvent



Scheme 1. Synthesis of the PEUs.

liquid systems (precipitation) or crystallization from solution as result of the solvent evaporation (casting) and melt crystallization at cooling (second DSC run and injection molding).

3. Results and discussion

3.1. Synthesis and characterization of the PEUs

Poly(ester-urethanes) are synthesized using poly(ϵ-caprolactone diol) as a soft segment and 1,1′-methylene-bis(4-isocyanatocyclohexane) and butanediol as components of the hard segment (Scheme 1).

Using this procedure, poly(ester-urethanes) with different length of PCL soft segment ($M_W = 2000, 4000, 7300$) are synthesized. The molecular weight (M_W) and chemical composition of PEUs is determined by GPC and ^{1}H NMR analyses. The molecular weight of the polymers and the content of PCL (wt%) are presented in Table 1. PEUs based on the shortest PCL segment ($M_W = 2000$) contain about 77 wt% PCL component and PEUs based on the longer PCL segments ($M_W = 4000$ and 7300) about 85 wt% PCL.

3.2. PEUs crystallized from solution

The thermal properties of PEUs are characterized by means of differential scanning calorimetry (DSC). The wide angle X-ray diffraction (WAXS) is used to investigate the crystalline phase of the PEUs.

All types of PEUs containing PCL as soft segment with molecular weight 2000, 4000 and 7300 are semicrystalline materials.

Fig. 1 presents and compares the wide angle X-ray diffractograms of selected PEUs with PCL-2000 (P2-33 and P2-60) and with PCL-4000 (P4-20 and P4-53). The samples are cast from solution at room temperature. It is clear that after 20 days storage at room temperature P4-20, P4-53, and P2-33 are partially crystallised, while WAXS of P2-60 shows only a broad diffusion scattering (amorphous halo) with maximum at $2\theta = 20°$. The position of the crystal reflection in the diffractograms of P4-20, P4-53, and P2-33 agrees well with those reported in the literature for polycaprolactone [35]. This result suggests that the crystalline phase which develops in the PEUs is associated with crystallization of the PCL soft segment.

Table 1 shows the thermal properties of PEUs, as obtained in a first DSC heating scan, and also reports the

Table 1
Thermal properties of the poly(ester-urethanes) and the starting poly(ϵ-caprolactones)

Sample Code	M_W PCL- unit	M_n	wt.% PCL	1st heating[b] (10°C min^{-1}) T_m (°C)	ΔH_m^a (J g^{-1})	α_c^a (%)	Cooling[b] (1°C min^{-1}) T_c (°C)	ΔH_c^a (J g^{-1})	2nd heating[b] (10°C min^{-1}) T_m (°C)	ΔH_m^a (J g^{-1})	α_c^a (%)	2nd heating after quenching[c] (20°C min^{-1}) T_m (°C)	ΔH_m^a (J g^{-1})	T_g (°C)	Δc_p (J g^{-1} °C)	MDSC[b] (2°C min^{-1}) T_g (°C)	Δc_p (J g^{-1} °C)
P2-33	2000	32 700	77,4	39	19	14	—	—	—	—	0	—	—	− 44	0.43	− 50	0.39
P2-54	2000	53 900	76,8	42	14	10	—	—	—	—	0	—	—	− 45	0.45	− 50	0.36
P2-60	2000	59 500	75,6	42	14	10	—	—	—	—	0	—	—	− 43	0.67	− 49	0.36
P4-20	4000	20 000	84,7	55	90	63	10	62	50	62	43	50	57	− 47	0.18	− 57	0.08
P4-36	4000	35 600	84,1	56	86	61	23	56	50	60	42	50	54	− 50	0.36	− 56	0.10
P4-53	4000	52 800	85,3	53	67	47	20	46	49	51	36	48	49	− 50	0.27	− 57	0.15
P7-61	7300	61 400	85,8	55	67	47	17	38	47	45	32	46	45	− 53	0.32	− 58	0.24
PCL		2000	100	53	85	60	30	72	46	74	52	50	71	− 60	0.31	− 69	0.17
PCL		4000	100	60	109	77	39	82	54	88	62	56	80	− 59	0.22	− 65	0.09
PCL		7300	100	60	108	76	41	77	55	81	57	n.d.	n.d.	n.d.	n.d.	− 65	0.08

[a] With respect to wt% PCL in PEU.
[b] Performed by MDSC, TA instrument.
[c] Performed by DuPont 9900 thermal analyzer.
n.d. = Not determined.

melting and glass transition parameters of polycaprolactone with $M_n = 2000$, 4000, 7300, which were used as soft blocks in the various PEUs.

The initial crystalline structure of PEUs is formed during precipitation from CH_2Cl_2 solution and storage at room temperature for more than 2 months. DSC data at first heating [Fig. 2(a) and (b), curve 2 and Table 1] indicate that the melting temperature, T_m, associated melting enthalpy, ΔH_m, and crystallinity, α_c, of PEUs are lower in comparison with T_m, ΔH_m and α_c of the PCL prepolymers [Fig. 2(a) and (b), curve 1 and Table 1]. The melting enthalpy ΔH_m is calculated with respect to the PCL content in PEUs. The crystallinity, α_c, of PCL phase is calculated using a value of ΔH_m for completely crystalline PCL, equal to 142 J g^{-1} [36]. T_m of PEUs containing PCL with lower molecular weight ($M_W = 2000$) shows higher depression (ΔT_m from 11° to 14°C)[1] than T_m of PEUs with PCL-4000 (ΔT_m from 4° to 7°C). The results indicate that the crystals obtained during crystallization from solution of the PCL soft segments in the PEU chain are less perfect than those developed in the initial PCL prepolymer. This is more clearly expressed in PEUs based on PCL-2000 soft segment due to the higher content of a hard segment in these polymers (Table 1).

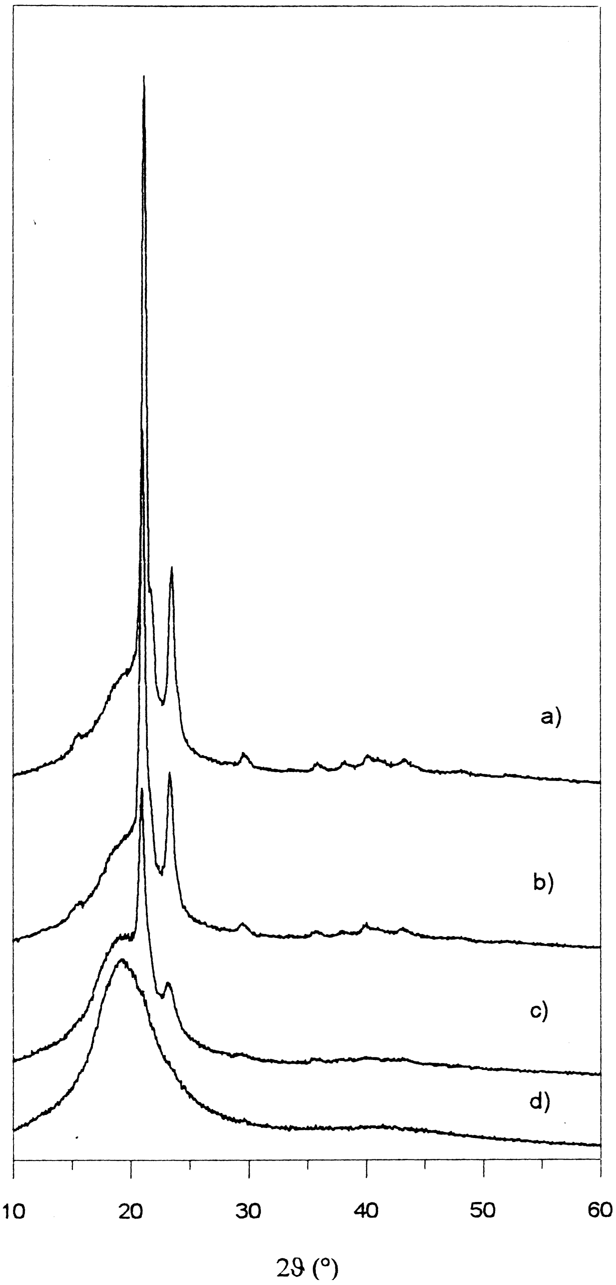


Fig. 1. WAXS spectra of P4-20(a), P4-53(b), P2-33(c), and P2-60(d).

The presence of chemical linkages between the hard and soft segments restricts the phase separation and ordering (crystallization) of PEUs. When the soft segment length increases from 2000 to 4000, the reduction in the degree of connectivity between the hard and soft segments should make the phase separation process and crystallization easier.

3.3. PEUs crystallized nonisothermally from melt

After the first heating more significant differences in the thermal properties of different types PEUs are observed. The PEUs based on PCL-2000 are completely amorphous after quenching at − 196°C from the molten state or even after slow cooling (1°C min^{-1}). The second DSC heating run of these samples shows only a T_g transition; no melting endotherm is observed [Fig. 2(a), curve 4]. When the PCL soft segment in PEUs has a higher molecular weight (4000 or 7300), crystallization occurs at cooling with rate of 1°C min^{-1} and even at quenching. The DSC curves of second heating show melting endotherms of the PCL crystalline phase in PEUs [Fig. 2(b), curve 2, Table 1]. The PCL prepolymers with different molecular weight give strong endotherms in the second heating run [Fig. 2(a) and (b), curve 3].

The melting temperature and enthalpy of second heating of PEUs based on PCL-4000 decrease in comparison with T_m and ΔH_m at first heating. Therefore, the crystallization of the PCL-segment from melt is less effective than the crystallization during precipitation from solution at room temperature (Table 1).

The decrease in crystallinity of the PCL phase in PEUs in comparison with the PCL homopolymer with the same molecular weight indicates a restriction of the crystallization of the PCL soft segments from the hard segments.

3.4. Glass-transition of PEUs

One of the advantages of the modulated DSC instrument used in this work is the determination of the glass transition of the amorphous phase in partially crystalline samples during a single DSC run. Table 1 reports the glass transition temperature (T_g) and change in the heat capacity (Δc_p) from the DSC curves obtained in a modulate heating. DSC results

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[1] $\Delta T_m = T_m^{\text{PCL homopolymer}} - T_m^{\text{PCL segment in PEU}}$.

show that the T_g of PEUs is higher than the T_g of the respective PCL prepolymers. This is also due to the contribution of the hard segment which decreases chain flexibility and consequently increases T_g. Increasing the hard segment content in PEUs based on PCL-2000 leads to a more pronounced increase in T_g ($\Delta T_g = 20°C$)[2] in comparison with PEUs based on PCL-4000 ($\Delta T_g = 9°C$).

Clear inverse correlation is observed between Δc_p and the crystallinity degree of the PEUs: the magnitude of the Δc_p at the glass transition of the amorphous phase is highest in the polymers with the lowest degree of crystallinity (P2-33, P2-54, and P2-60). When DSC scans are carried out after quenching from a melt or after continuously cooling with 1°C min^{-1} P2-33, P2-54, and P2-60 do not crystallize and in a subsequent scan no melting endotherm is observed (Table 1). For these PEUs Δc_p is between 0.43 and 0.67 J g^{-1} °C, values that correspond to the specific heat increment of the totally amorphous polymers (compare with Δc_p of partially crystalline samples obtained by MDSC).

Table 2
Crystallinity of various poly(ester-urethanes) determined by WAXS analysis 20 days after casting from solution

Code	$M_{W\ \text{PCL-unit}}$	M_n	χ_c (%)
P2-33	2000	32 700	14
P2-54	2000	53 900	16
P2-60	2000	59 500	0
P4-20	4000	20 000	35
P4-36	4000	35 600	31
P4-53	4000	52 800	29
P7-61	7300	61 400	28

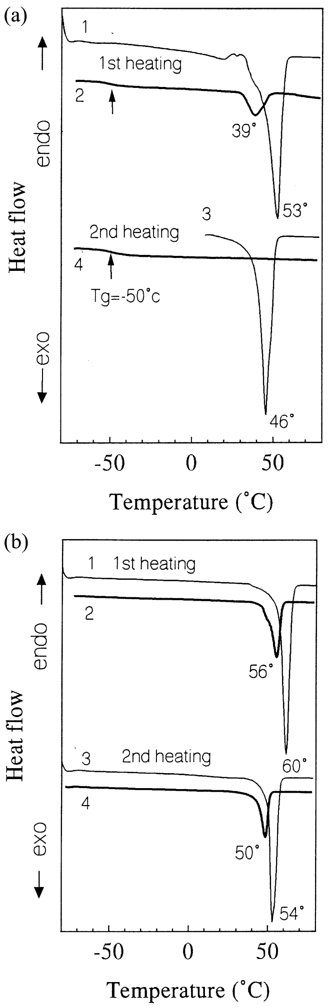

Fig. 2. (a) DSC heating curves (10°C min^{-1}) of PCL-2000 (curves 1 and 3) and P2-33 (curves 2 and 4). Curves 1 and 2 — 1st heating; curves 3 and 4 — 2nd heating after cooling at 1°C min^{-1}. (b) DSC heating curves (10°C min^{-1}) of PCL-4000 (curves 1 and 3) and P4-36 (curves 2 and 4). Curves 1 and 2 — 1st heating; curves 3 and 4 — 2nd heating after cooling at 1°C min^{-1}.

3.5. Crystallinity of PEUs: effect of the M_W of PCL segment, total M_W of PEUs and concentration of the hard segment

From the X-ray and DSC results it is clear that the initial PEUs with the shortest PCL block ($M_n = 2000$) exhibit the lowest degree of crystallinity. It is quite reasonable that crystallization is inhibited by shortening of the crystallizable block, owing to enhanced number of connections between soft and hard segments (at equal molecular weight of PEUs). The effect of the PCL block length on crystallizability of the PEUs seems to vanish with increasing length of the block. As a matter of fact P7-61, whose PCL block length is almost twice that of P4-53, does not show a sensibly higher crystallinity. The present results suggest that block length affects crystallizability only when the block becomes shorter, i.e. with molecular weight less than 4000.

Apart from the length of the PCL block, crystallizability of the PEUs seems to be also affected by the total molecular weight of the polymer, as illustrated by comparison of P4-20 and P4-53 (see Table 1). The two PEUs have the same PCL block length and PCL content, but P4-20 has a remarkably lower molecular weight than P4-53 (20 000 vs 52 800).

The data of the degree of crystallinity, χ_c, from X-ray analysis in Table 2 and the degree of crystallinity, α_c, DSC determined in Table 1 show that among PEU with long PCL blocks (PCL-4000) the highest degree of crystallinity is reached by the PEU with the lowest molecular weight (P4-20).The same effect does not clearly show up in PEUs based on PCL-2000 (compare P2-33 with P2-54) owing to the intrinsic difficulty of PEUs with short PCL blocks to crystallize, that has been discussed above.

The degree of crystallinity (χ_c) of solution-cast PEU samples, estimated from the X-ray diffractograms (Table 2), decreases in the order: P4-20 $>$ P4-36 $>$ P4-53 $\cong$ P7-61 $>$ P2-54 $\cong$ P2-33 $\gg$ P2-60. The higher molecular weight of PEU and concentration of hard segments leads to restriction of crystallization of the PCL segments in PEUs. P2-60 crystallizes only after more than two months storage at room temperature.

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[2] $\Delta T_g = T_g^{\text{PCL homopolymer}} - T_g^{\text{PEU}}$.

Table 3
Isothermal crystallization of poly(ester-urethanes) (MW of PCL segment = 4000)

Code	M_n	T_c (°C)	τ_c^{max} (s)	Avrami parameters n	z	$\tau_{0.5}$ (s)
P4-20	20 000	20[a]	96	—	—	—
		25	198	3.1	3.5×10^{-8}	222
		30	486	3.6	1.1×10^{-10}	504
P4-36	35 600	20[a]	132	—	—	—
		25	246	3.6	1.2×10^{-9}	270
		30	540	3.9	8.0×10^{-12}	570
P4-53	52 800	20[a]	186	—	—	—
		25	594	4.2	8.1×10^{-13}	636
		30	1740	n.d.	n.d.	n.d.
PCL	4000	25[a]	6	—	—	—
		30[a]	12	—	—	—
		40	132	2.5	1.4×10^{-6}	186
		45	1626	3.1	8.5×10^{-11}	1578

n.d. = not determined.
[a] Partial crystallization begins during cooling to T_c.

The degree of crystallinity, χ_c, evaluated by WAXS, shows lower values than the degree of crystallinity, α_c, determined by DSC. The reason for this difference is that χ_c is evaluated as the ratio between the crystalline PCL phase scattering and the whole X-ray scattering of the sample (including the crystalline PCL diffraction and the amorphous diffraction of PCL and hard segments), while in DSC analysis α_c represents the crystallinity of the PCL phase only.

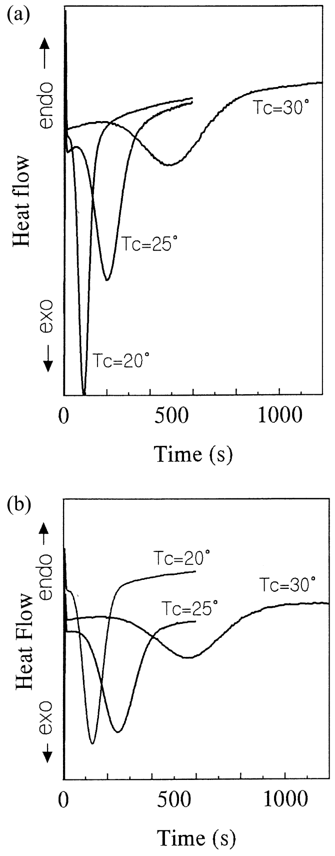


Fig. 3. (a) DSC curves for the isothermal crystallization of P4-20. (b) DSC curves for the isothermal crystallization of P4-36.

3.6. Isothermal crystallization of the PEUs: equilibrium melting temperature

In order to obtain more detailed information about the influence of the PEU molecular weight on the crystallizability of the soft segment an isothermal crystallization of PEUs was performed. The isothermal crystallization of PEUs based on PCL-4000 is carried out in the temperature range from 15° to 40°C. Because of the great difference in crystallizability of PEUs in comparison with the initial PCL, the common crystallization temperature range is rather narrow — from 25° to 30°C.

Fig. 3(a) and (b) allows comparison of the DSC curves of isothermal crystallization of P4-20 and P4-36, containing PCL-4000 as a soft segment.

In general, with increasing temperature of the isothermal crystallization, T_c, the crystallization rate, corresponding to the reciprocal of the peak time of the exotherm, τ_{max}, decreases [Fig. 3(a) and (b), Table 3]. At the same temperature of isothermal crystallization (25 or 30°C), τ_{max} increases, i.e. the rate of crystallization decreases with increasing molecular weight of PEUs (Table 3).

Melting temperatures, T_m, of PCL prepolymer (PCL-4000) and PCL segments in PEUs are measured as a function of the crystallization temperature, T_c. As expected the melting temperature, T_m, increases with the crystallization temperature, T_c. The extrapolation of the observed melting temperatures to the line $T_m = T_c$ has been frequently used in order to obtain the equilibrium melting temperature of many homopolymers and different copolymers [37–45].

However, there are a few recent studies on crystallization kinetics of linear polyethylene and random copolymers of polyethylene which show that the conventional extrapolative method failed for the random copolymers at low levels of crystallinity, or extrapolation to a reasonable equilibrium melting temperature can be carried out only with data obtained at intermediate crystallization temperature [40,41]. Unfortunately, in these papers which present interesting and non-expected results, the conditions for cooling from the molten state to the crystallization temperature are not exactly specified. It is known that this is a very important step in an isothermal crystallization experiment to prevent or minimize the nonisothermal crystallization during cooling to certain crystallization temperature. In this paper we investigate the PEUs composition dependence of the apparent equilibrium melting temperature for higher levels of crystallinity.

The equilibrium melting temperature, T_m^o, is obtained by Hoffman–Weeks extrapolation method, [37] i.e. by extrapolation of the least-square fit of T_m data to the reference line $T_m = T_c$ [Fig. 4(a)–(d)].

It was noticed that the crystallization of PCL prepolymer

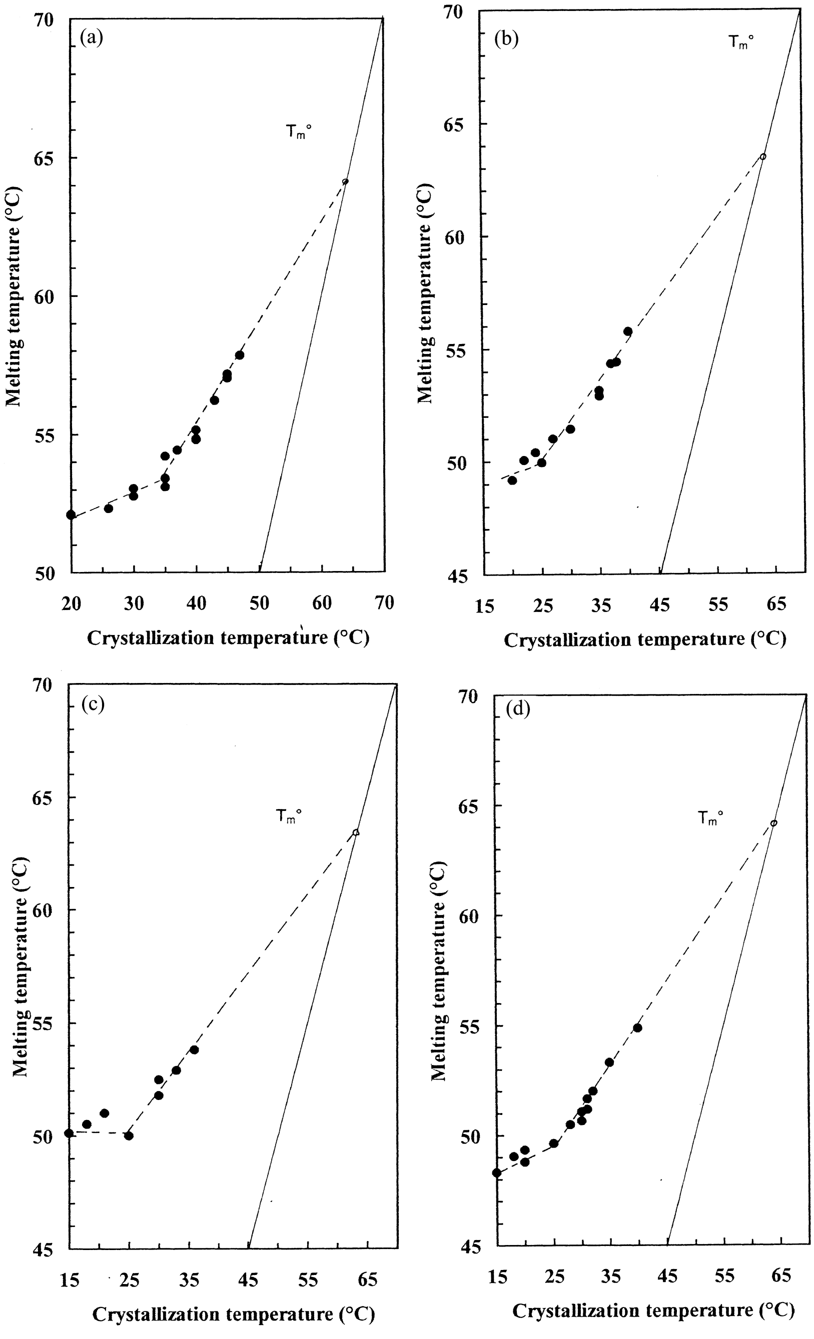


Fig. 4. Dependence of melting temperature (T_m) of isothermally crystallised PCL-4000(a), P4-20(b), P4-53 (c) and P4-36(d) on crystallization temperature (T_c).

and PCL segments in PEU is sufficiently rapid at high undercooling, to begin before reaching T_c at the cooling rate employed. This occurs with PCL-4000 prepolymer below 40°C and with PCL segments in PEUs below 25°C. This is one of the reasons why the T_m–T_c dependence in the Hoffman–Weeks plots shows a slope change below these temperatures [Fig. 4(a)–(d)]. The observed dependence also arises from annealing during the heating scan which causes an improvement in crystal quality and hence a T_m increase, particularly evident in samples crystallized at low T_c.

The equilibrium melting temperature, T_m^o, obtained from the plots of Fig. 4(a) for pure PCL-4000 is 64.2°, in agreement with literature results on PCL with similar molecular weight [46].

The apparent equilibrium melting temperatures, T_m°, for the PCL segments in PEUs containing PCL-4000 lay in the range 63.3–63.6°C, which is slightly lower than that of pure PCL. This is reasonable to expect and can be explained by the chemical bonding between PCL soft segment and hard segments that decreases the length of PCL segment which is capable to crystallize. It is known that the equilibrium melting temperature decreases with decreasing of the molecular weight of the polymers [46,47].

3.7. Crystallization kinetics of PEUs

The isothermal crystallization kinetics of PEUs is interpreted in terms of the Avrami equation [48,49].

$$\alpha(t) = 1 - \exp(-z \cdot t^n) \quad (1)$$

where $\alpha(t)$ is a mass fraction of polymer crystallized at time t, n is an exponent which contains contributions related to the crystal growth geometry and the nucleation type, z is an overall crystallization rate constant involving contributions from crystal growth and nucleation.

The half time of crystallization, $\tau_{0.5}$, rate constant of crystallization, z, and Avrami parameter, n, are determined and presented in Table 3. The half crystallization time $\tau_{0.5}$ is related to the rate constant and can be determined from the Avrami expression as:

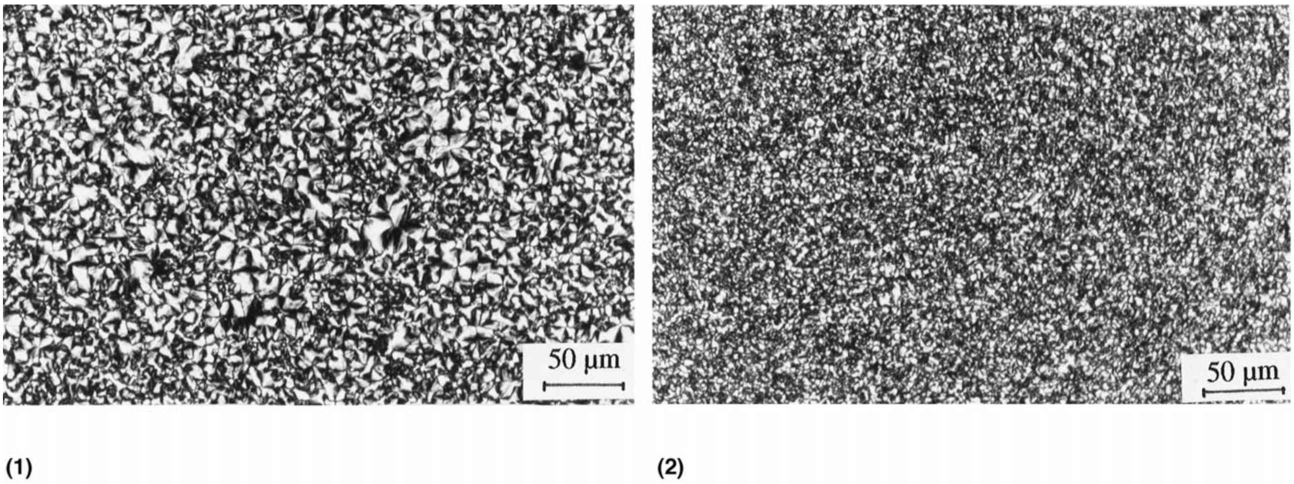
$$\tau_{0.5} = (\ln 2/z)^{1/n} \quad (2)$$

The crystallization of PCL-4000 prepolymer is very fast at high undercoolings (25 and 30°C) and — at the cooling rate employed — partially occurs before reaching the crystallization temperature. The same happens — though to a lower extent — in the PEUs at $T_c = 20$°C. At higher T_c, the crystallization of PEUs occurs extremely slowly in comparison with the PCL prepolymer. For example, at 25°C the half crystallization time, $\tau_{0.5,}$ is more than 220 s (Table 3). As can be seen in Table 3 the PCL-4000 prepolymer has a similar value for the half crystallization time, $\tau_{0.5}$, (186 s) at a significantly higher temperature of crystallization, $T_c = 40$°C. The data of Table 3 show that, at the same crystallization temperature, there is a measurable increase of $\tau_{0.5}$ and a corresponding decrease of the rate constant, z, with increasing total molecular weight of the PEUs.

These results confirm that the rate of crystallization of PCL soft segments in PEUs is much lower than the rate of crystallization of the initial PCL and depends on the total molecular weight of PEUs.

The crystallization of PEUs is described by the Avrami equation with an exponent n ranging from 3 to 4, which indicates spherulitic growth.

The different crystallizability of PEUs is confirmed by light microscopy as well. The initial PCL-2000 and PCL-4000 form spherulite structures from solution after evaporation of the solvent and from melt at cooling to certain T_c. PEUs based on PCL-4000 crystallize very fast with the evaporation of the solvent. P4-20 forms relatively large spherulite structure (20–30μm) (Fig. 5, micrograph 1), while P4-53 gives fine spherulite structure with an average spherulite size of about 2–4 μm (Fig. 5, micrograph 2). At the same time the PEU P2-33 (based on PCL-2000) forms



(1) (2)

Fig. 5. Optical microscope photographs (crossed polaroids) of solution-cast P4-20 (micrograph 1) and P4-53 (micrograph 2), taken 1.5 h after solvent evaporation at room temperature.

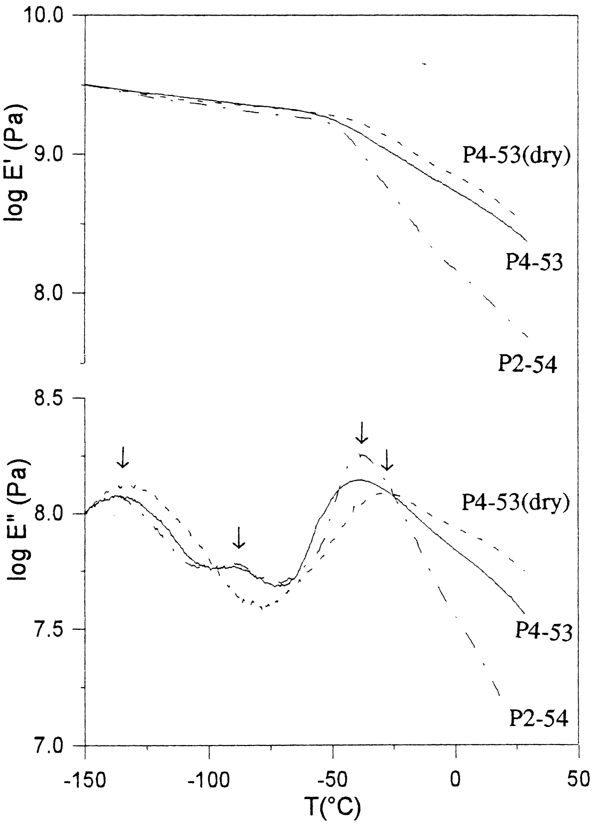


Fig. 6. DMTA curves of PEUs: P2-54 (– · –) and P4-53 (——) in 'room humidity' conditions; P4-53 (- - -) after drying under vacuum over P_2O_5.

crystals over 3 days after evaporation of the solvent, P2-54 after 5 days, and P2-60 does not crystallize even after 20 days storage at room temperature.

PEUs crystallize more slowly at cooling from melt to room temperature than from a solution. P4-20 forms spherulites which grow to 2–3 μm after 20 hrs of isothermal crystallization at 40°C. After 65 days storage (annealing) at room temperature, all PEUs show spherulite structure with different sizes, which are smaller for PEUs based on PCL-2000 than for PEUs based on PCL-4000.

3.8. Dynamic mechanical thermal analysis of PEUs

The viscoelastic properties of PEUs based on both PCL-2000 and PCL-4000 were characterized by means of dynamic mechanical thermal analysis (DMTA). DMTA allows different types of transitions and relaxations to be detected and related to the structure and morphology of the segmented PEUs studied. The DMTA can be used to study the influence of dissolved water in segmented PEUs as well [50].

Fig. 6 shows the dynamic mechanical spectra from -150°C to room temperature of P2-54 and P4-53. In correspondence with the glass transition at about -40°C, the dynamic storage modulus, E', drops and the loss modulus, E'', shows a maximum. The foregoing differences of crystalline phase content of the PEUs are also reflected by the DMTA spectra. Since the curves of Fig. 6 refer to partially crystalline PEUs, the elastic modulus at the glass transition shows a relatively modest drop as a result of the rigidity imparted by the crystals above T_g. As expected, this effect is stronger in P4-53, which has a higher degree of crystallinity.

In addition to the glass transition, the viscoelastic spectra of P2-54 and P4-53 show an evident low temperature relaxation at about -135°C, which is also present in PCL and was attributed early on [51] to local motions of the methylene sequences. Between the low temperature relaxation and the glass transition another mechanical dispersion region is found in the 'room conditioned' samples at about -90°C. A similar relaxation phenomenon was observed in various poly(ester-urethanes) by Jacobs and Jenckel [52], who also reported its water dependence [53]. This transition can be attributed to β-relaxation [53] of the PEUs caused by the rotation of the short segments in the main chain of the amorphous domains. A number of polyesters [54,55], including PCL (M. Scandola, unpublished results), also show a water-dependent relaxation in a comparable temperature range. In the PEUs presently investigated it was found that the relaxation at about -90°C is closely related with the presence of small amounts (0.2–0.3 wt%) of absorbed water; the relaxation disappeares from the spectrum upon extensive drying, and reappeares upon re-exposure to normal room humidity conditions. As an example, Fig. 6 compares the spectra obtained with P4-53 after room humidity conditioning and after drying under vacuum over P_2O_5. The main changes observed upon drying are the disappearance of the intermediate relaxation at -90°C and the shift to higher temperature of the glass transition. The latter effect is clearly related to loss of the ubiquitous plasticizer, water, which lowers the glass transition of the PEUs exposed to normal room humidity conditions.

4. Conclusions

The morphology and physical properties of segmented poly (ester-urethanes) are studied in connection with the soft segment length, content of the hard segment and total molecular weight. It is established that all PEUs containing a PCL soft segment with different molecular weight are crystallizable polymers. They present a heterogeneous structure consisting of a continuous PCL matrix with a hard segment dispersed rigid phase. WAXS results show that the crystalline phase which develops in PEUs is associated with PCL soft segment crystallization.

DSC data, obtained at first heating run, indicate that all PCL soft segments with different length form a crystalline structure during precipitation from solution. A less perfect crystallization of PCL soft segment than the crystallization of initial PCL prepolymers is observed. That is more clearly expressed in PEUs based on PCL with the lowest length

($M_W = 2000$). The chemical linkage (connectivity) between the hard and soft segments restricts the phase separation and crystallization of the PCL soft segment.

A more significant difference in the morphology and thermal properties of different types PEUs is observed for the samples which are cast from a solution or cooled after the first melting. The PEUs based on the shortest PCL soft segment ($M_W = 2000$) are completely amorphous immediately after solvent evaporation, or after quenching from molten state, or even after slow cooling from a melt. When the PCL soft segment has a higher molecular weight ($M_W =$ 4000 or 7300) crystallization occurs rapidly during evaporation of the solvent or at cooling from melt and even at quenching.

It is established that the crystallizability of the segmented PEUs is also affected by the total molecular weight of the polymers. The data from WAXS and DSC analysis show that PEUs with a lower total molecular weight reach a higher crystallinity. Therefore, the higher molecular weight of the PEU and higher concentration of the hard segment lead to restriction of the PCL soft segment crystallization.

The results from isothermal crystallization kinetics and light microscopy analysis confirm the different crystallizability of segmented PEUs depending on their composition and molecular weight.

The results from modulated DSC indicate an increase of glass transition temperature, T_g, of segmented PEUs in comparison with T_g of PCL prepolymers, due to the decrease of chain flexibility imparted by the hard segments.

Dynamic mechanical spectroscopy of selected samples of segmented PEUs shows, in addition to the glass transition, an evident low temperature relaxation at -135°C which is attributed to local motions of the methylene sequences in the PCL soft segments and a water-dependent relaxation at -90°C.

The results obtained show that the structure formation and properties of PEUs depend on the different procedures for sample preparation (precipitation, casting from solution and melt crystallization), due to the different crystallization conditions for the PCL soft segments. It is anticipated that the different morphology of PEUs will affect their enviromental degradation. The biodegradibility of PEUs is under investigation and it will be described and discussed in the next paper.

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References

[1] Seymour RW, Cooper SL. Macromolecules 1973;6 (1):48.
[2] Chang YJP, Wilkers GL. J Polym Sci, Polym Phys Ed 1975;13:455.
[3] Van Bogart JWC, Bluemke DA, Cooper SL. Polymer 1981;22:1428.
[4] Koberstein JT, Gancarz I. J Polym Sci, Polym Phys 1986;B24:2487.
[5] Turner RB, Christenson CP, Harthcock MA, Howard WL, Creswick MW. Polymeric materials science and engineering, In: Proceedings of the ACS Division of Polymeric Materials Science and Engineering, vol. 58. Washington, DC: ACS, Books and Journals Division, 1988:947.
[6] Kazmierczak ME, Fornes RE, Buchanan DR, Gilbert RD. J Polym Sci, Polym Phys 1989;B27:2173.
[7] Kazmierczak ME, Fornes RE, Buchanan DR, Gilbert RD. J Polym Sci, Polym Phys 1989;B27:2189.
[8] Hun SL, Shaw LH. Macromolecules 1989;22:1100.
[9] Sreenivasan K. Eur Polym J 1991;27 (8):811.
[10] Koberstein JT, Leung LM. Macromolecules 1992;25:6205.
[11] Chu B, Gao T, Li Y, Wang J, Desper CR, Byrne CA. Macromolecules 1992;25:5724.
[12] Kim BK, Lee YM. Colloid Polym Sci 1992;270 (10):956.
[13] Li Y, Gao T, Chu B. Macromolecules 1992;25:1737.
[14] Wilkers GL, Bagrodia S, Humphries W, Wildnauer R. Polymer Lett 1975;13:321.
[15] Van Bogart JWC, Gibson PE, Cooper SL. J Polym Sci, Polym Phys Ed 1983;21:65.
[16] Xiao F, Shen D, Zhang X, Hu S, Xu M. Polymer 1987;28:2335.
[17] Shilov VV, Blyznyuk VN, Lipatov YuS. J Mater Sci 1987;22 (5):1563.
[18] Xiao F, Zang X, Hu S, Ma D, Luo X, Xu M. Chin J Polym Sci (Engl Ed) 1988;6 (1):84.
[19] Beumel LL. Polym Mater Sci Eng 1989;61:565.
[20] Ma D, Mao R, Luo X, Xu M. Chin J Polym Sci (Engl Ed) 1990;8 (4):353.
[21] Spathis G, Kontou E, Kefalas V, Apekis L, Christodoulides C, Pissis, P, Ollivon M, Quinquenet S. J Macromol Sci Phys 1990;B29 (1):31.
[22] Yuying X, Dening W, Chunpu H, Shengkang Y, Junxian L. J Appl Polym Sci 1993;48 (5):867.
[23] Ferguson J, Patsavoudis D. Eur Polym J 1987;8:385.
[24] Abouzahr S, Wilkes GL, Ophir Z. Polymer 1982;23:1077.
[25] Hwang KKS, Hemker DJ, Cooper SL. Macromolecules 1984;17:307.
[26] Estes GM, Cooper SL, Tobolsky AV. J Macromol Sci Rev, Macromol Chem 1970;C4:167.
[27] Koutsky JA, Hien NV, Cooper SL. J Polym Sci 1970;B8:353.
[28] Clough SB, Schneider NS, King AO. J Macromol Sci, Phys 1968;2:641.
[29] European Community Specific Programme for Research, Technological Development and Demonstration in the Field of Agriculture and Agro-Industry, including Fisheries. Biodegradability of bioplastics: Prenormative research, Biorecycling, and Ecological Impacts. AIR 2-CT93-1099, internal report, Brussels, 1997.
[30] Toncheva V, Van Den Bulcke A, Schacht E, Mergaert J, Swings J. J Environ PolymDegradation 1996;4 (2):71.
[31] Zhu Y, Huang Y. Polymer Mater Sci Engng 1994;10 (3):80.
[32] Toncheva V, Schacht E, Bogdanov B, De Reu B. Gordon Research Conference on Biodegradable Polymers, ‘Il Ciocco’. Barga, Italy, 1997.
[33] Schindler A, Hibionada M, Pitt CG. J Polym Sci, Polym Chem Adv 1982;20:319.
[34] Loccufier J, Van Bos M, Schacht E. Polym Bull 1991;27:201.
[35] Bittiger H, Marchessault RH. Acta Crystallogr 1970;1923:B26.
[36] Wunderlich B. In: Macromolecular physics, vol. 3, crystal melting. New York: Academic Press, 1980:54.
[37] Hoffman JD, Weeks JJ. J Res Natl Bur Stand US 1962;66:13.
[38] Murphy CJ, Fag JJ, Vail EAM, Sperling LH. J Appl Polym Sci 1993;48 (8):1321.
[39] Goulet L, Prud’ Homme RE. J Polym Sci, Polym Phys 1990;B28:2329.
[40] Alamo RG, Chan EKM, Mandelkern L, Voigt-Martin IG. Macromolecules 1992;25 (24):6381.
[41] Alamo RG, Viers BD, Mandelkern L. Macromolecules 1995;28:3205.

[42] Thomann R, Sernetz FG, Heinemann J, Steinmann S, Mülhaupt R, Kresseler J. Macromolecules 1997;30:8401.

[43] Hamley IW, Fairclought JPA, Bates FS, Ryan A. Polymer 1998;39 (6–7):1429.

[44] Floudas G, Tsitsilianis C. Macromolecules 1997;30:4381.

[45] Seo SW, Ha WS. J Appl Polym Sci 1993;48:833.

[46] Chen HL, Li LJ, Ou Yang WC, Hwang JC, Wong WY. Macromolecules 1997;30:1718.

[47] Booth C, Price C. In: Comprehensive polymer science, the synthesis, characterization, reaction and applications of polymers, polymer properties, vol. 2. Oxford: Pergamon Press, 1989:407.

[48] Avrami MJ. Chem Phys 1939;7:1103.

[49] Avrami MJ. Chem Phys 1940;8:212.

[50] Starstev OV, Iordannski AL, Zaikov GE. Polym Degradation Stab 1987;17 (4):273.

[51] Koleske JV, Lundberg RD. J Polym Sci 1969;2 (7):795.

[52] Jacobs H, Jenckel E. Makromol Chem 1961;43:132.

[53] Jacobs H, Jenckel E. Makromol Chem 1961;47:72.

[54] Ceccorulli G, Pizzoli M, Scandola M. Polymer Comm 1986;27:228.

[55] Scandola M, Pizzoli M, Ceccorulli G, Cesaro A, Paoletti S, Navarini L. Int J Biol Macromol 1988;10:373.