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Stereocomplex formation in enantiomeric diblock and triblock copolymers of poly (ε-caprolactone) and polylactide

Sandrine Pensec*, Maïna Leroy, Hakim Akkouche, Nicolas Spassky

Laboratoire de Chimie des Polymères, UMR 7610, Université Pierre et Marie Curie,
4 Place Jussieu, 75252 Paris Cedex 05, France

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Summary

Enantiomeric diblock and triblock copolymers from caprolactone and lactide with various compositions were synthesized using alcohol/tin octoate as initiator system.
Stereocomplexes were formed between pairs of enantiomeric block copolymers and their thermal properties examined. The melting temperatures of the crystalline PCL and PLA phases are depending on the composition of block copolymers. A raise of approximately 55°C of the temperature of PLA phase is observed in the blends as a consequence of stereocomplex formation as well in diblock as in triblock copolymers.

Introduction

The formation of a stereocomplex by blending enantiomeric macromolecules has been studied for example on polythiiranes (1, 2), polyoxiranes (3), polylactones (4, 5) and more recently of polylactides (PLA) (6, 7). The co-crystallization of enantiomeric polymeric chains leads to a racemic crystalline lattice structure which is different from the homopolymer crystallite (8). The properties of such racemic blends are very different from that of parent homopolymers. For example a raise of 50°C is observed in the melting point of stereocomplexes compared to the optically pure polymers. Stereocomplexes from poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) has been extensively studied during the past decade (6, 7, 9, 10). Polymers based on lactides and lactones are interesting materials for use in medical, pharmaceutical, environmental and ecological applications (11, 12, 13).

Block copolymers from lactide (LA) and ε-caprolactone (CL) containing crystalline and amorphous blocks afford materials with versatile properties and can also be used as compatibilizers in blends of homopolymers. Such block copolymers can be synthesized by different techniques using coordination-insertion initiators, e.g., bimetallic μ-oxo alkoxide (14), aluminum isopropoxide (15), rare earth alkoxide (16, 17, 18) or anionic initiator (19). It was reported that stereocomplex formation occurs by blending PCL-b-PLLA and PCL-b-PDLA block copolymers (18, 20).

As concerning triblock copolymers containing lactide and ε-caprolactone sequences, a synthesis based on the reactivated PCL-PLA-OAl diblock copolymer was proposed (21). Triblock PLA-PCL-PLA copolymer with long lactide sequences has been recently described (22).

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* Corresponding author

In this paper we would like to report our recent results on the formation of stereocomplexes from different diblock and triblock enantiomeric PLA-PCL copolymers and on the variation of thermal properties in function of the composition of the latter.

Experimental

Materials

L-lactide and D-lactide were provided by Purac Biochem and purified by sublimation under vacuum. ε-Caprolactone (Aldrich) was distilled under high vacuum. Polycaprolactone diol (M_n = 3900 g.mol^{-1}) was provided by Solvay and used as received. Distilled stannous octoate was a gift from Michel Vert. Ethanol (99,85% for analysis, Normapur from Prolabo) was dried over molecular sieves 4Å. ^{1}H and ^{13}C NMR spectra were carried out with a Brucker AC200 spectrometer. $CDCl_3$ was used as a solvent. SEC measurement were carried out in THF as an eluent using a Waters 510 pump, a LDC analytical refractometer and four PL gel columns (10^4, 10^3, 500 and 100 Å). Calibration was effected with polystyrene standards. Molecular weights were determined according to the universal calibration principle. DSC measurements were performed with a Tainstrument MDSC 2920. The samples were heated at the rate of 20°C/min.

Polymerization procedure

The synthesis of ε-caprolactone prepolymers was performed in flask purged with dry argon and equipped with a magnetic stirrer. The monomer/ethanol ratio varied from 20 to 80 according to desired M_w of prepolymer. The monomer/tin octoate was maintained as 1000. The polymerization was run in bulk 22 h at 110°C. At the end of polymerization, the polymer was dissolved in dichloromethane and then poured in cold methanol. The precipitation was repeated two times. Then the polymer was dried 48 h under vacuum and analyzed.

The copolymerizations were performed exactly in the same way, the hydroxylated caprolactone prepolymer or the polycaprolactone diol playing the role of alcohol with corresponding adjustment of reagents.

Results and discussion

Synthesis of block copolymers

Two strategies can be applied for the synthesis of block copolymers.

The first approach is directly relied to the living character of the polymerization process, consists to perform a sequential addition of a desired monomer on the living growing chain end of a first monomer. This strategy was applied for the synthesis of PCL-b-PLLA and PCL-b-PDLA diblock copolymers (19). However it is not possible by this technique to obtain triblock copolymers since PLA end chain is not able to initiate the polymerization of CL.

For this reason another strategy was used in which a prepolymer with a functional end group, e.g., a hydroxyl group, is prepared, then a second monomer is added in the presence of a catalyst. Generally in this case the control of molar masses is not fully assumed. However recently, PCL-b-PLA diblock copolymers were prepared with tin octoate/alcohol system in satisfactory controlled conditions (23).

Using $Sn(Oct)_2/EtOH$ system in which EtOH plays the rule of initiator and $Sn(Oct)_2$ is the catalyst, we have prepared in a first step PCL's of different degrees of polymerization (DP). Then in a second step, using the hydroxyl terminated PCL's as initiator and $Sn(Oct)_2$ as catalyst, we have prepared by bulk polymerization at 110°C PCL-b-PLLA and PCL-b-PDLA diblock copolymers. The composition of block copolymers was varied by taking different initial ratios of LA/PCL. This method allowed us also to prepare the corresponding triblock PLLA-b-PCL-b-PLLA and PDLA-b-PCL-b-PDLA copolymers by using a dihydroxy PCL prepolymer.

The results of enantiomeric PCL-b-PLLA diblock copolymers synthesis are given in Table 1. Almost identical results were obtained in the case of synthesis of PCL-b-PDLA diblock copolymers.

Table 1. Molecular characteristics of PCL-b-PLLA diblock copolymers prepared in bulk polymerization.

N°	DP_{CL}(a)	$DP_{calc\ LA}$(b)	$DP_{exp\ LA}$(c)	$M_{n,PCL}$(d) $\times 10^{-3}$	$M_{n,exp\ diblock}$(e) $\times 10^{-3}$	M_w/M_n(e)
1	41	41	36	9.3	18.7	1.20
2	62	54	62	13.6	25.2	1.20
3	54	20	19	11.9	17.9	1.30
4	68	20	17	14.7	21.7	1.30
5	106	20	23	22.4	26.3	1.40

Polymerizations carried out in bulk at 110°C during 22 h. Conversion 100%

(a) DP is calculated from the real $M_{n\ PCL}$ obtained according to (26) from the $M_{n\ exp\ PCL}$ measured using polystyrene standards

(b) calculated from the ratio LLA/prepolymer PCL-OH (in moles)

(c) experimental value calculated from integration of PCL and PLLA signals in ^1H NMR spectrum of block copolymer. Number of LA repeat units in the PLLA block

(d) PCL prepolymer: SEC in THF; polystyrene standards

(e) block copolymer: SEC in THF; polystyrene standards

Diblock copolymers were characterized by several techniques.

SEC analysis demonstrated an increase in molecular weight after polymerization of LA on PCL-OH prepolymer. A single polymer peak was formed with a narrow molecular weight distribution (MWD) which corroborate the successful synthesis of block copolymers and the absence of homopolymers.

In ^1H NMR spectra the ratio of methine LA signals at 5.14 ppm versus methylene CL signals at 4.02 ppm allows to determine the composition in LA and CL units in copolymers. ^{13}C NMR spectra show only two single peaks in the carbonyl region at 173.5 and 169.5 ppm assigned respectively to LA and CL sequences. This confirm the diblock character of copolymers and the absence of transesterification reactions. Typical ^1H and ^{13}C NMR spectra are shown in Fig. 1.

A satisfactory fitting is observed between expected and experimentally found DP's in lactide blocks.

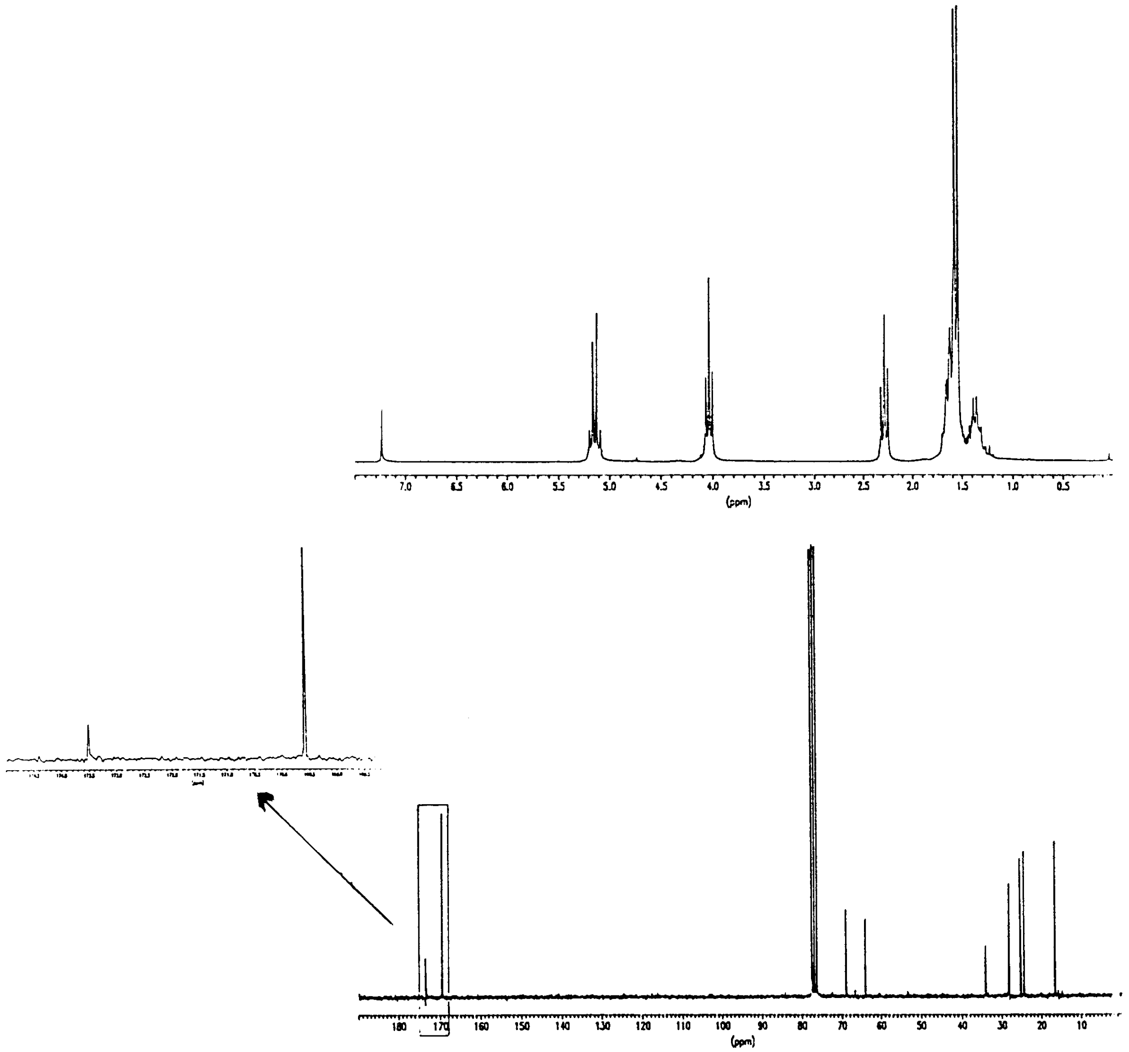

Figure 1. ^{1}H and ^{13}C NMR spectra of an enantiomeric diblock copolymer PCL-b-PLLA in $CDCl_3$ solutions

Two enantiomeric triblock copolymers were prepared and starting from a caprolactone diol prepolymer (M_n = 3900 g.mol^{-1}). The characteristics of triblock copolymers are presented in Table 2.

Table 2. Synthesis of PLA-b-PCL-b-PLA triblock copolymers

N°	$DP_{exp\ LA}$$^{(c)}$	$M_{n,exp\ triblock}$$^{(d)}$ $\times 10^{-3}$	$M_w/M_n$$^{(d)}$	Yield (%)
TL1$^{(a)}$	80	28.0	1.13	86
TD1$^{(b)}$	82	28.8	1.13	88

Polymerizations run in bulk at 110°C during 22 h. [LA]/[$Sn(Oct)_2$] = 1000 [LA]/[PCL-diol] = 56

$^{(a)}$ L-lactide, $^{(b)}$ D-lactide, $^{(c)}$ calculated from ^{1}H NMR spectra

$^{(d)}$ SEC in THF; polystyrene standards

The structure of triblock copolymers was substantiated likely to the case of diblock copolymers by the raising of MW in SEC traces and the nature of signals in ^1H and ^{13}C NMR spectra. In the following text we shall see that DSC thermograms by the bias of melting points demonstrate the occurrence of lactide block with a DP close to 28 in agreement with a triblock LA(28)-b-CL(34)-b-LA(28) type structure.

Thermal properties of block copolymers

DSC measurements were performed on all prepared diblock and triblock enantiomeric copolymers and their blends. Melting temperatures T_m and melting enthalpies (ΔH) of some typical diblock enantiomeric copolymers and their blends are presented in Table 3.

Table 3. Thermal properties of enantiomeric PCL-b-PLA diblock copolymers and their stereocomplexes

N°	DP_{CL}	DP_{LA}	$T_{m\ PCL}$ (°C)	ΔH_{PCL} (J/g)	$T_{m\ PLA}$ (°C)	ΔH_{PLA} (J/g)
1L	41	34	50.0	32	158.0	34
1D	41	36	50.2	29	157.0	30
1L+1D			49.1	28	211.1	48
3L	54	19	54.1	46	144.4	16
3D	55	20	55.1	39	139.2	19
3L+3D			55.3	45	202.5	31
5L	106	23	54.6	57	141.2	14
5D	106	21	53.8	56	146.4	14
5L+5D			53.9	61	199.1	19

In Fig. 2 are given DSC traces of copolymers 1L, 1D and their blend. Sharp single peaks are observed.

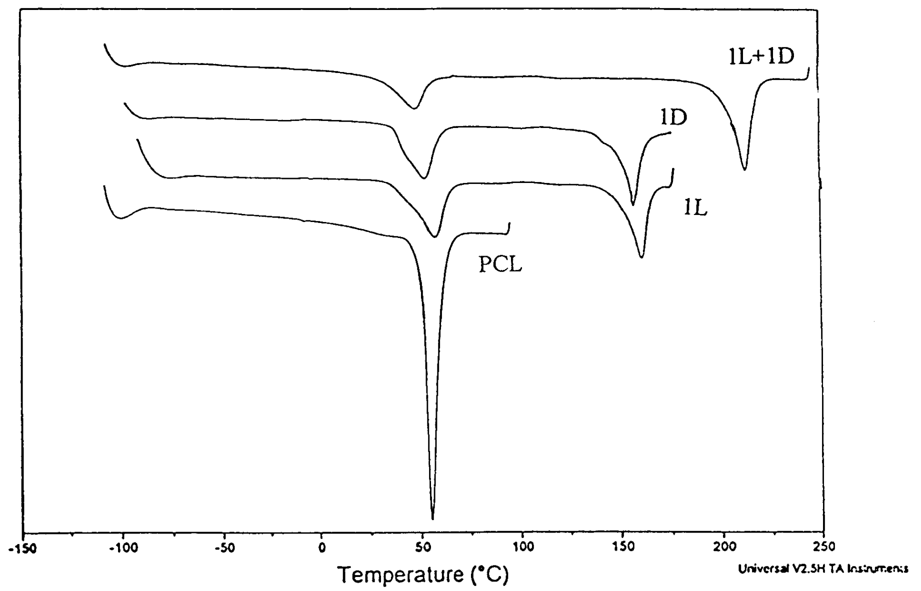

Figure 2. DSC traces of block copolymers 1L, 1D and their blend. Heating rate 20°C/min.

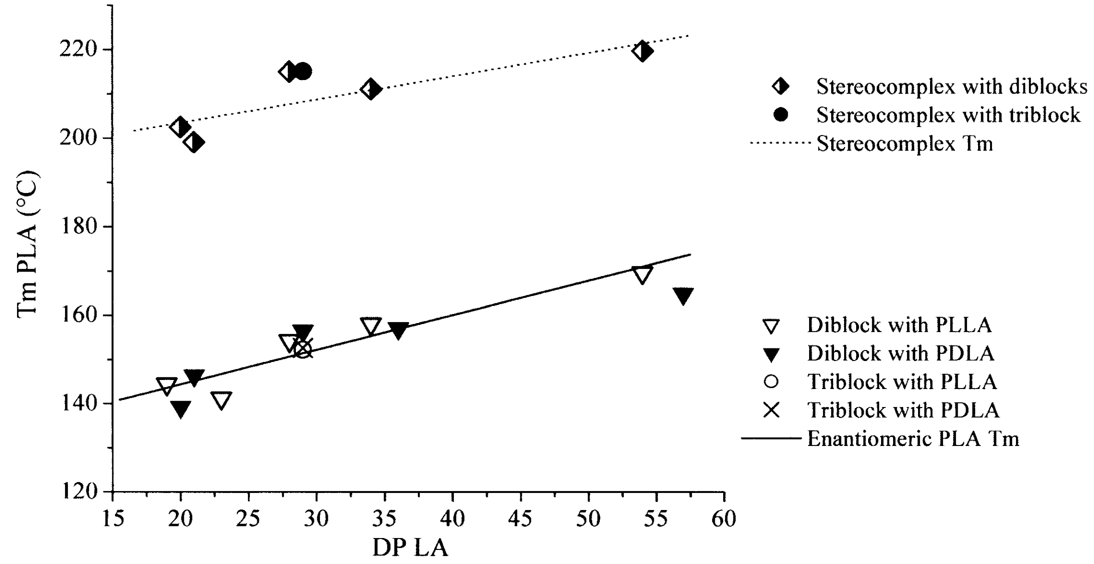

Figure 3. T_m of enantiomeric PLA and PLLA/PDLA blends as a function of degree of polymerization, data taken from Table 3 and 4

All the examined copolymers were found to be crystalline. The melting points of CL and LA blocks depend on respective DP's. T_m variation of lactide block versus DP is plotted in Fig. 3. T_m increase in function of DP. A similar trend was previously observed for pure poly(L-lactide)s (24). It is interesting to note that T_m of stereocomplexes increase in an almost parallel way. T_m of stereocomplexes are approximately 55°C higher than that of enantiomeric copolymers.

Enthalpies are also depending on molecular weights. In the case of stereocomplexes a strong raise of melting enthalpy of PLA phase is observed, while the enthalpy of PCL phase is almost unaffected. This may be explained by a higher degree of crystallinity in the stereocomplex. Similar behavior in function of composition of diblock copolymers was reported by Stevels et al (17).

The thermal properties of triblock copolymers were compared with two particular diblock copolymers as shown in Table 4.

Table 4. Thermal properties of enantiomeric triblock copolymers (T), related diblock copolymers (6,7) and their stereocomplexes (S)

N°	$M_{n,PCL}$ $\times 10^{-3}$	$M_{n,PLA}$ $\times 10^{-3}$	DP_{CL}	DP_{LA}	$T_{m\ PCL}$ (°C)	ΔH_{PCL} (J/g)	$T_{m\ PLA}$ (°C)	ΔH_{PLA} (J/g)
TL	3.9	8.4	34	58	-	-	152.2	39
TD	3.9	8.4	34	58	-	-	152.6	41
ST					-	-	215.1	61
6L	2.7	4.0	24	28	43.1	25	154.2	40
6D	2.7	4.2	24	29	45.5	24	156.5	39
S6					46.2	-	215	59
7L	4.6	7.8	40	54	51.6	22	169.6	42.5
7D	4.6	8.2	40	57	54.7	15	164.9	44
S7					50.4	18	219.7	55

It appears that triblock copolymers lactide phase T_m of TL and TD are very close to that observed in 6L and 6D diblock copolymers (152-154°C) which bear block of 29 lactide units, but quite different of that of 7L and 7D (T_m = 165-170°C) which bear sequences of 57 units. Thus it is reasonable to assume that the triblock is set up of two blocks with 29 LA units surrounding a middle block of PCL. It is worthy to note that the latter do not show crystallinity (Fig. 4). Such a behavior was recently reported in the case of PLA-PEG-PLA triblock copolymers in which the middle block segment of polyethyleneglycol (PEG) do not recristallize either in enantiomeric triblock copolymers as well as in their blends (25). It is worthy to note that T_m of enantiomeric triblocks and their blend are fitting well on linear relationships established for diblock copolymers (Fig. 3).

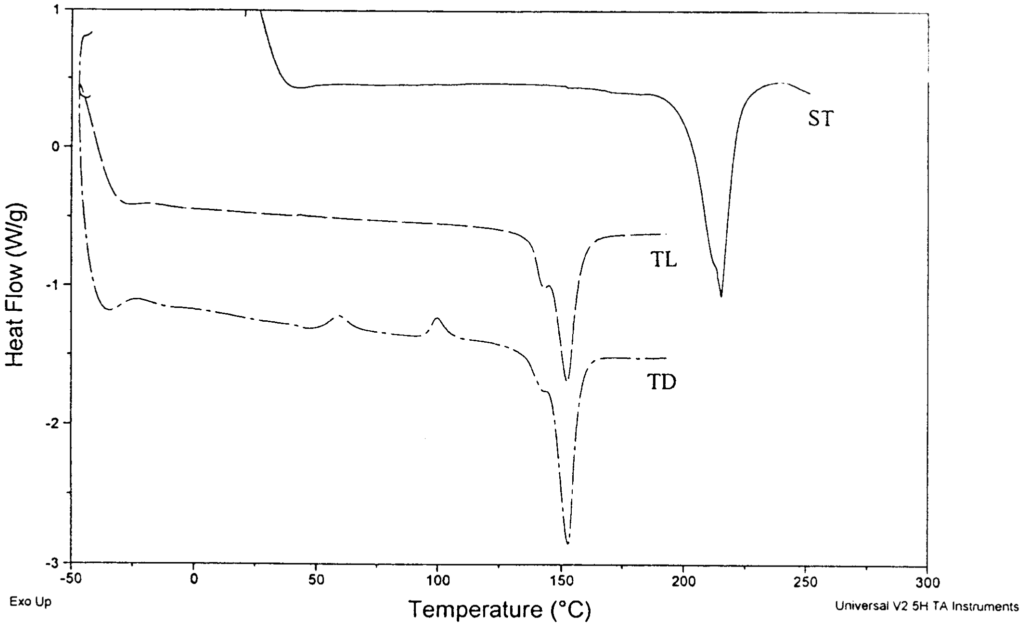

Fig. 4: DSC traces of enantiomeric triblock copolymers TL, TD and their blend ST. Heating rate 20°C/min.

Conclusion

Thermal properties of CL and LA diblock and triblock copolymers of different composition and the corresponding blends were examined. The stereocomplex formed between a pair of enantiomeric diblock or triblock copolymer exhibited a higher melting crystalline temperature. The magnitude of melting temperatures is depending on DP's of lactide sequences but seems to be unaffected by the length of CL block. Further studies on triblock copolymers are in progress.

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References

1. Dumas P, Spassky N, Sigwalt P (1972) Makromol Chem 156:95
2. Matsubayshi H, Chatani Y, Tadokoro H, Dumas P, Spassky N, Sigwalt P (1977) Macromolecules 10:996
3. Sakakihara H, Takakashi Y, Tadokoro H, Oguni N, Tani H (1973) Macromolecules 6:205
4. Lavallée C, Grenier D, Prud’homme R-E, Le Borgne A, Spassky N (1985) Synthesis and properties of racemic and optically active substituted poly(β-propiolactones). In: Culbertson B-M and Mc Grath J-E (eds) Advances in Polymer Synthesis, Plenum Publ Corp p 441
5. Voyer R, Prud’homme R-E (1989) Eur Polym J 25:365
6. Ikada Y, Jamshidi K, Tsuji H, Hyon S-H (1987) Macromolecules 20:904 and references following
7. Murdoch J-R, Loomis G-L (1988) US Patent 4719246, US Patent 4766182; (1989) US Patent 4800219
8. Tadokoro H (1981) Makromol Chem Suppl 4:129
9. Brochu S, Prud’homme R-E, Barakat I, Jerôme R (1995) Macromolecules 28:5230
10. Brizzolara D, Cantow H-J, Diederichs K, Keller E, Domb A-J (1996) Macromolecules 29:191
11. Vert M, Li S-M, Spenlehauer G, Guérin P (1992) J Mater Sci Mater Med 3:432
12. Sinclair R-G (1996) J Macromol Sci Pure Appl Chem Suppl 5:30
13. Ikada Y, Tsuji H (2000) Macromol Rapid Comm 21:117
14. Feng X-D, Song C-X, Chen W-Y (1983) J Polym Sci Polym Lett Ed 21:593
15. Jacobs C, Dubois P, Jerôme R, Teyssié Ph (1991) Macromolecules 24:3027
16. Stevels W-M, Ankoné M-J-K, Dijkstra P-J, Feijen J (1996) Macromolecules 29:3332
17. Stevels W-M, Ankoné M-J-K, Dijkstra P-J, Feijen J (1996) Macromol Symp 102:107
18. Simic V, Pensec S, Spassky N (2000) Macromol Symp 153:109
19. Bero M, Adamus G, Kasperczyk J, Janeczek (1993) Polym Bull 31:9
20. Spassky N, Pluta C, Simic V, Thiam M, Wisniewski M (1998) Macromol Symp 128:39
21. Song C-X, Feng X-D (1984) Macromolecules 17:2764
22. Maglio G, Migliozzi A, Palumbo R, Immirzi B, Volpe M-G (1999) Macromol Rapid Comm 20:236
23. In’T Veld P-J-A, Velner E-M, Van de Witte P, Hamhuis J, Dijkstra P-J, Feijen J (1997) J Polym Sci Part A Polym Chem 35:219
24. Jamshidi K, Hyon S-H, Ikada Y (1988) Polymer 29:2229
25. Lim D-W, Park T-G (2000) J Appl Polym Sci 75:1615
26. Dubois Ph, Barakat I, Jérôme R, Teyssié Ph (1993) Macromolecules 26:4407