Synthesis of Poly(vinyl alcohol)-*graft*-poly(ε-caprolactone) and poly(vinyl alcohol)-*graft*-poly(lactide) in Melt with Magnesium Hydride as Catalyst

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ABSTRACT: Grafting of poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) chains on poly(vinyl alcohol) backbone (PVA degree of hydrolysis 99%) was investigated using MgH_2 environmental catalyst and melt-grown ring-opening polymerization (ROP) of ε-caprolactone (CL) and L-lactide (LA), that avoiding undesirable toxic catalyst and solvent. The ability of MgH_2 as catalyst as well as yield of reaction were discussed according to various $PVA/CL/MgH_2$ and $PVA/LA/MgH_2$ ratio. PVA-*g*-PCL and PVA-*g*-PLA were characterized by ^{1}H- and ^{13}C-NMR, DSC, SEC, IR. For graft copolymers easily soluble in tetrahydrofuran (THF) or chloroform, wettability and surface energy of cast film varied in relation with the length and number of hydrophobic chains. Aqueous solution of micelle-like particles was realized by dissolution in THF then addition of water. Critical micelle concentration (CMC) decreased with hydrophobic chains. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1188–1197, 2009

Key words: graft polymer; poly(ε-caprolactone); polylactide; poly(vinyl alcohol)

INTRODUCTION

In the past few years, many research works have been devoted to the synthesis of well-defined structure such as block, comb, or star polymers based on biocompatible and biodegradable aliphatic polyesters. The control of the macromolecular structure led to versatile polymers with optimized chemical, physical, and mechanical properties. Such polymers have been mainly developed in biomedical and pharmaceutical fields for gel development and tissue engineering.[1] Further applications could be as plasticizers and compatibilizing agents for industrial polymers and packaging materials.[2] By increasing the production and uses of materials from such polymers, the necessity to safeguard our environment became a target for further development of green chemistry. Thus, it became essential to optimize the synthesis of each polymer and especially to get rid of the undesirable toxic molecules as catalysts and solvents because complete removal of residue from the solid is quite impossible. New catalysts as well as bulk and melt polymerization process need to be developed.

Aliphatic polyesters such as poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) were first synthesized from anionic or coordination-insertion ring-opening polymerization (ROP) of monomers in the presence of alkali metals or organometallic compounds, carboxylates and alkoxides as typical and effective initiators.[3–5] Non-toxic Ca, Fe, and Mg based catalysts or co-initiator are preferable. Recently, ROP was investigated, for example, in the presence of calcium alkoxide,[6] ferric alkoxide,[7] ferrous acetate,[8] and natural amino acids[9] considering that the biocompatibility and *in vivo* safety of thus-obtained polymers must be satisfying for medical and pharmaceutical purpose.

Amphiphilic diblock and triblock copolymers were synthesized from hydrophilic mono or α,ω-dihydroxy-poly(ethylene oxide) (PEO) used as initiator. The hydrophobic polyester block(s) resulted from ROP of ε-caprolactone (CL), β-butyrolactone (BL), glycolide (GL), and lactide (LA). Among the various catalysts (SnO, PbO, GeO_2, $SnCl_2$...) experienced to prepare the PEO based-initiator,[10,11] Zn^{12} and calcium ammoniate[13] seems to be the least toxic. However, the one most commonly catalyst used was the commercially stannous 2-ethylhexanoate or stannous octoate ($Sn(Oct)_2$) because it allowed to high polymerization rate and it was accepted by the Food and Drug Administration.[14] However the cytotoxycity of $Sn(Oct)_2$ against a broad variety of microorganisms is undesirable when tin salt is present as

impureties in polymers designed for medical or pharmaceutical applications.[15]

Branched and star-shaped polymers were prepared by using alcohols with different numbers of hydroxyl groups as initiators and to date, $Sn(Oct)_2$ was used as catalyst. Polyester-based structures growing from glycerol, pentaerythrol, polyglycerine,[16] and dipentaerythrol[17] have been described. It was suggested that high hydroxyl content, like in multi-hydroxyl functional polymers, should accelerate polymerization of lactone and lactide by increasing the number of growing chains. Multi-hydroxyl functional backbones offer also the possibility of building different architectures, therefore the physicochemical properties such as hydrophilic–hydrophobic balance could be controlled by the type and amount of backbone used. Recently, a novel synthetic method was developed by the use of poly(L-lactide) (PLLA) extended chains resulting from the hydrolytic degradation of PLLA crystallized films. Extended chains are anticipated to act as a initiator system with $Sn(Oct)_2$ because they have many hydroxyl groups.[18]

Typical and interesting architectures are comb-like branched polyesters. Little is known about the synthesis and the properties of such copolymers. Poly (vinyl alcohol) (PVA) backbone was used as macroinitiator for ROP of CL and LA in solution in the presence of $Sn(Oct)_2$. The choice of non-toxic polymerization solvents is strongly limited because of the poor solubility of PVA, except in water. The ring-opening oligomerization of CL with PVA was examined in an aqueous solution at 120°C,[19] however, no graft copolymer was obtained. PVA-*graft*-PCL (PVA-*g*-PCL) and PVA-*graft*-PLA (PVA-*g*-PLA) were synthesized in dimethylsulfoxide (DMSO)[19] and in N,N'-dimethylformamide (DMF)/toluene solvent system respectively.[20] PVA-*g*-PLA was also synthesized via ring-opening melt polymerization. For this, PVA (molecular weight 10,000–15,000 and degree of hydrolysis 80–88%), $Sn(Oct)_2$, L-lactide or D,L-lactide were mixed at 130°C and clear melt was obtained by the authors.[21] Possible dissolution of PVA in monomer was probably due to the residual non-hydrolyzed acetate groups (12–20%) in backbone material. Patents on the preparation of similar graft copolymers by bulk or melt polymerization have been already published, however no clear description of the process was done.[22,23]

Synthesized PVA-*g*-PCL and PVA-*g*-PLA continue to receive increasing interest particularly in biomedical sector. Amphiphilic comb copolymers can self-disperse in certain solvents which are good solvents for backbone and poor solvents for graft chains. A combination between PVA, PCL, and PLA chains is attractive in terms of the formation of spherical nonionic micelles and hydrogels for applications in encapsulation and drug delivery systems.

In the present article, we report the melt-grown synthesis of PVA-*g*-PCL and PVA-*g*-PLA from PVA totally hydrolyzed, using magnesium hydride (MgH_2) as a new catalyst for the preparation of PVA based-initiator for ROP of lactone and lactide. MgH_2 was selected because magnesium is involved in human metabolism and it is an environmental metal. Thus, it was supposed that non-toxic impurities were left in the copolymer. The objective of our research is to show the efficiency of MgH_2 and to characterize the chemical structure of the graft copolymers by changing the polymerization conditions. In addition, to demonstrate the amphiphilic character of synthesized copolymers we investigated the hydrophilic–hydrophobic surface properties of copolymer cast films and the preparation of micelle-like particles in aqueous solution.

EXPERIMENTAL

Materials

PVA (molecular weight M_w = 41,000 g mol^{-1}, M_n = 28,000 g mol^{-1}, degree of hydrolysis 99%) dissolved with heat in lactone and lactide monomers. Dissolution was strongly dependent on the monomer/PVA ratio and was improved by addition of dimethyl sulfoxyde (DMSO). PVA was rigorously dried at 100°C *in vacuo* for at least 6 h. ε-caprolactone (CL, b.p. 96–97.5°C/10 mm Hg) was dried on CaH_2 and distilled. L-Lactide (LA, m.p. 92–94°C) was purified by crystallization from dried toluene then sublimate. Chiral L-LA monomer was selected for current investigation into the stereochemistry of the polymerization. Complete results will be published shortly. In this article, polylactide block is called PLA without reference to the possible stereoregularity of the polymer chain. Dimethyl sulfoxyde (DMSO) was dried under CaH_2 and purified by repeated distillation under reduced pressure over CaH_2. Magnesium hydride (MgH_2) was used as received. X-rays analysis of dry MgH_2 revealed the presence of following elements (in at.%, after deducting oxygen from analysis under air): Mg 99.38, Ca 0.1, Al 0.38, Si 0.12, Fe 0.01. PVA, monomers, DMSO and MgH_2 were stored under argon. All chemicals were provided by Sigma-Aldrich.

Measurements

^{1}H- and ^{13}C-NMR were recorded in $CDCl_3$ or DMSO d_6 at 25°C with a Bruker spectrometer at 400 and 100 MHz respectively. Chemical shifts are given in ppm downfield from TMS. Differential Scanning Calorimetry (DSC) was carried out with a Metler DSC 30 instrument in sealed aluminium pans under nitrogen atmosphere. The heating rate was 10°C/min, profiles covered a range from −100 to 250°C. Size exclusion chromatography (SEC) was

performed on Waters HR3, HR4, and HR5 columns with Waters 515 pump, Waters 2410 RI detector, eluent chloroform, flow rate 0.5 mL/min. FTIR spectra were recorded with a Perkin Elmer 100 spectrometer. Cast films were prepared from 5 to 10% w/w solution of copolymers in THF. Contact angles of cast films were measured 5 s after the drop was deposited with a Kruss G1 apparatus. Surface energy (γ_s), dispersive (γ_s^d), and polar (γ_s^p) components were calculated with the Owens and Wendt method using water and diiodomethane.[24]

The following equations were used:

$$(1 + \cos\theta)\gamma_l = 2(\gamma_s^d\gamma_l^d)^{1/2} - 2(\gamma_s^p\gamma_l^p)^{1/2}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

(θ contact angle with water or diiodomethane, surface tension, polar and dispersive components for water: $\gamma_l = 72.8$ mJ m^{-2}, $\gamma_l^p = 51.0$ mJ m^{-2}, $\gamma_l^d = 21.8$ mJ m^{-2} and for diiodomethane: $\gamma_l = \gamma_l^d = 44.6$ mJ m^{-2}.

Micelle-like particles in aqueous solutions of copolymers were prepared by slow addition, dropwise, of doubly distilled water into THF solutions of copolymers with stirring. THF was slowly removed using a rotary evaporator at 25°C for 2 h. CMC was deduced from the graph of surface tension (mJ m^{-2}) of aqueous solution of copolymers versus the polymer concentration (Log$C$ g/L). Surface tensions were measured at 25°C with a Lauda tensiometer. Surface tension decreased with increasing the concentration below CMC and it is nearly constant above CMC. CMC was then taken as the change in slope of the graph.

Synthesis of PVA-*g*-PCL

Weighing out of chemicals and synthesis were run in a glove box to avoid humidity and oxygen traces. As an illustrative example, PVA grinded to a powder with a pestle (PVA unit 3.15 mmol, 0.1386 g), CL (13.88 mmol, 1.582 g) and finely powdered MgH$_2$ (0.2 mmol, 0.0052 g) were introduced in a round-bottomed flask (50 mL) equipped with an efficient bar magnet. The mixture was slowly stirred for 2 h at ambient temperature and degassed *in vacuo*. The flask was kept under dry argon and immersed in a silicone oil bath at 150°C for about 16 h. Chloroform was added to complete dissolution of crude product (one night under stirring) and to separate non-reacted PVA. Solution was poured down slowly in methanol (two times). Precipitated copolymer was collected by filtration and dried *in vacuo* at ambient temperature. Yield in copolymer was dependent on continuous stirring of reaction mixture and heating time. High viscosity was noticed after 2 h and yield was optimized by heating up to 36 h. However for some feed compositions, the mixture was slightly brownish because of thermal degradation of non-reacted PVA and PVA backbone of the copolymer. Some attempts were done to lower the temperature. A strongly reduced coloration or even no coloration was noticed at 110°C under argon but yield was cut down by 20–30%.

Synthesis of PVA-*g*-PLA

Same general procedure as described earlier was used. Some modifications were required because of the limited dissolution of PVA in melt LA at 150°C, particularly for LA/PVA ratio smaller than about 7 (in mmol, or 23 in weight). As an illustrative example, PVA grinded to a powder with a pestle (PVA unit 1.05 mmol, 0.0462 g), LA (13.88 mmol, 1.998 g) and finely powdered MgH$_2$ (0.2 mmol, 0.0052 g) were introduced in a round-bottomed flask (50 mL) equipped with an efficient bar magnet. The mixture was slowly stirred for 2 h at ambient temperature and degassed *in vacuo*. The flask was kept under dry argon and immersed in a silicone oil bath at 175°C for 30 min to obtain a clear melt, then at 150°C for about 16 h. The crude copolymer was purified by dissolution in chloroform and precipitation in methanol, solid product was dried *in vacuo* at room temperature. By heating up to 36 h, yield was lightly increased but browning of the solid appeared. For every 10°C decrease in reaction temperature, colouration gets down gradually. 110°C temperature led to high drop in yield but absence of colouration. Addition of DMSO resulted in more easy dissolution of PVA in small amounts of melt LA and ensured good yield for the graft copolymerization. PVA (4.54 mmol, 0.2 g) and LA (3.47 mmol, 0.5 g) were heated at 100°C, DMSO (12.8 mmol, 1 mL) then MgH$_2$ (0.38 mmol, 0.01 g) were added. The flask was heated at 150°C for about 16 h. Dissolution and precipitation of the product followed the same above procedure. Particular care was needed to eliminate DMSO totally from solid copolymer by prolonged drying *in vacuo* at mild temperature.

Determination of conversion % of monomers

Experiments were conducted for example with PVA 1.13 mmol, CL 10.41 mmol, MgH$_2$ 0.38 mmol at 150°C (run 5 Table I). Samples from crude products of PVA-*g*-PCL were analyzed by ^{1}H-NMR. The time-dependence was followed by the appearance of the methine proton signal of the grafting linkage PVA—CH$_2$—CH—OCO—PCL at 5.08 ppm. Imprecise NMR identification of CL and PVA signals in crude products led to very rough determination of non-reacted amounts and monomer conversion therefore. Crude products were dissolved and precipitated then yield

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TABLE I
Properties of PVA-*g*-PCL from Melt-Synthesis Using MgH$_2$ as Catalyst

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Run no.	Feed ratio (mmol) PVA[a] unit	CL	MgH$_2$	Solvent DMSO mmol	PVA-*g*-PCL DP$_{exp}$[b]	DP$_{th}$[b]	DS$_{exp}$[c] %	DS$_{th}$[c] %	T_g[d] °C	T_m[d] °C	Yield[e] (PCL)[f] wt %
1	1.85	13.88	0.06		5.9	115.6	–	6.5	−40	60	60
2	3.15	13.88	0.20		8.1	34.7	4.9	12.7	−50	54	69 (53)
3	10.60	13.88	0.24		–	28.9	–	4.5	−32	–	20
4	1.13	6.94	0.38		4.6	9.1	16.7	67.2	−58	40	76 (68)
5	1.13	10.41	0.38		5.4	13.7	29.4	67.2	−60	45	65 (78)
6	1.13	13.88	0.38		6.8	18.3	24.3	67.2	−61	46	80 (81)
7	0.92	1.68	0.03		–	28	–	6.5	−35	–	35
8	1.05	1.68	0.20		1.2	4.2	13.3	38	−32	–	30 (30)
9	1.85	1.68	0.05		–	16.8	–	5.4	−30	–	5
10	8.02	7.98	0.20		3.4	19.9	–	4.9	−30	–	22
11	1.13	4.38	0.38	6.4	–	5.8	31.1	67.2	−56	–	85
12	1.59	4.38	0.38	6.4	3.1	5.8	18.3	47.8	−54	–	75 (60)
13	2.25	4.38	0.38	6.4	2.1	5.8	12.2	33.7	−34	–	88 (40)
14	4.58	4.38	0.38	6.4	3.7	5.8	9.8	16.6	−34	–	84 (49)

[a] PVA degree of hydrolysis 99%, M_w = 41,000 g mol^{-1}.
[b] Experimental [DP$_{exp}$ from NMR spectra and eq. (2)] and theoretical [DP$_{th}$ from eq. (4)] degree of polymerization of grafted PCL chains based on ε-caprolactone monomer unit ─CO(CH$_2$)$_5$O─.
[c] Experimental [DS$_{exp}$ from NMR spectra and eq. (1)] and theoretical [DS$_{th}$ from eq. (3)] degree of substitution of PVA backbone chains (percentage of grafted PVA units).
[d] Glass transition temperature (T_g) determined for first heating run and melting temperature (T_m). PCL: T_g = −65°C and PVA: T_g = 68°C.
[e] Yield in weight % of precipitated PVA-*g*-CL to PVA and CL in initial feed. Crude product was slowly dissolved in chloroform then precipitated in methanol.
[f] PCL content in weight % from eqs. (9) and (10).

in % weight was determinate. NMR analyses of copolymer were done for each sample with about 15 mg of copolymer in 1 mL CDCl$_3$. A better estimate of conversion % of CL was obtained by comparing the intensity of methine proton signal and weight %.

Same procedure was followed for PVA-*g*-PLA: PVA 1.05 mmol, LA 13.88 mmol, MgH$_2$ 0.2 mmol at 150°C (run 3 Table II). The time-dependence was followed by the appearance of the methine proton signal of the grafting linkage PVA─CH$_2$─C$\underline{H}$─OCO ─PLA at 5.35 ppm and the disappearance of the methine proton signal of non-reacted LA at 5.10 ppm.

Determination of degree of substitution and degree of polymerization

Experimental degree of substitution (DS$_{exp}$) of PVA backbone by PCL grafted chains and experimental degree of polymerization (DP$_{exp}$) of PCL grafted chains were estimated from ^{1}H-NMR spectra by eqs. (1) and (2):

$$DS_{exp} = 2I_{5.08}/(I_{1.2-1.8} - 3I_{2.30}) \quad (1)$$

$$DP_{exp} = I_{2.30}/I_{2.65} \quad (2)$$

Theoretical degree of substitution (DS$_{th}$) and theoretical degree of polymerization (DP$_{th}$) were estimated by eqs. (3) and (4):

$$DS_{th} = 2[MgH_2]/[PVA\ units] \quad (3)$$

$$DP_{th} = [CL]/2[MgH_2] \quad (4)$$

For PVA backbone grafted by PLA chains, equations are following:

$$DS_{exp} = I_{5.40}/(I_{5.40} + I_{3.86})$$
$$= 2I_{5.40}/[I_{1.1-1.7} - 3(I_{5.16} + I_{4.20})] \quad (5)$$

$$DP_{exp} = (I_{5.16} + I_{4.20})/I_{4.20} \quad (6)$$

$$DP_{th} = 2[LA]/2[MgH_2] \quad (7)$$

M_n of the copolymer was estimated by eq. (8):

$$M_n = M_{nPVA} + [(M_{m.u} \times DP_{exp})(DS_{exp} \times M_{nPVA}/44)] \quad (8)$$

with M_{nPVA} number molecular weight of PVA and $M_{m.u}$ molecular weight of monomer unit ─CO(CH$_2$)$_5$O─ or ─COCH(CH$_3$)O─.

PCL and PLA weight % were estimated by eqs. (9) and (10):

$$M_{w\,of\,PCL\,or\,PLA} = DS_{exp} \times DP_{exp} \times M_{m.u} \times M_{wPVA}/44 \quad (9)$$

$$wt\% = M_{w\,of\,PCL\,or\,PLA}/M_{w\,PVA} + M_{w\,of\,PCL\,or\,PLA} \quad (10)$$

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TABLE II
Properties of PVA-*g*-PCL from Melt-Synthesis Using MgH$_2$ as Catalyst

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Run no.	Feed ratio (mmol)			Solvent	PVA-*g*-polylactide							
	PVA[a] unit	LA	MgH$_2$	DMSO mmol	DP$_{exp}$[b]	DP$_{th}$[b]	DS$_{exp}$[c] %	DS$_{th}$[c] %	T_g[d] °C	T_m[d] °C	Yield[e] (PLA)[f] wt %
1	0.53	13.88	0.20			69.4		75.5	43	–	74
2	1.05	13.88	0.20		7.9	69.4	15.8	38.1	48	–	70 (67)
3	2.10	13.88	0.20			69.4		19.1	44	–	70
4	3.15	13.88	0.20			69.4		12.7	42	–	35
5	5.34	13.88	0.20			69.4		7.5	40	–	22
6	10.5	13.88	0.65			21.3		12.4	40	–	10
7	1.13	3.47	0.38		8.2	9.1	17.9	67.2	50	115	38 (71)
8	1.13	4.86	0.38		8.2	12.8	22.3	67.2	48	–	35 (75)
9	1.13	6.94	0.38		9.6	18.3	23.6	67.2	49	118	65 (79)
10	1.13	10.41	0.38			27.4		67.2	46	–	64
11	1.13	3.47	0.38	6.4		9.1		67.2	54	112	78
12	1.59	3.47	0.38	6.4		9.1		47.8	54	–	62
13	2.27	3.47	0.38	12.8	8.5	9.1	18.3	33.5	48	122	70 (72)
14	4.54	3.47	0.38	12.8		9.1		16.7	46	130	76

[a] PVA degree of hydrolysis 99%, M_w = 41,000 g mol^{-1}.
[b] Experimental [DP$_{exp}$ from NMR spectra and eq. (7)] and theoretical [DP$_{th}$ from eq. (9)] degree of polymerization of grafted polylactide chains based on L-LA monomer unit —COCH(CH$_3$)O—.
[c] Experimental [DS$_{exp}$ from NMR spectra and eq. (6)] and theoretical [DS$_{th}$ from eq. (8)] degree of substitution of PVA backbone chains (percentage of grafted PVA units).
[d] Glass transition temperature (T_g) determined for first heating run and melting temperature (T_m) for maximum heat of broad peak area on wide temperature range about 60°C. PLA: T_g = 57°C and PVA: T_g = 68°C.
[e] Yield in weight % of precipitated PVA-*g*-CL to PVA and LA in initial feed. Crude product was slowly dissolved in chloroform then precipitated in methanol.
[f] PLA content in weight % from eqs. (9) and (10).

RESULTS AND DISCUSSION

The control of hydrophilic–hydrophobic balance of graft PVA is required to promote recent applications. For environmental considerations, PCL and PLA chains were selected to be grafted by ROP of CL and LA using a clean melt process with non-toxic MgH$_2$ catalyst. To investigate the possibility for MgH$_2$ to catalyst the reaction and to allow the control of the copolymer structure in such conditions, runs with various PVA/CL/MgH$_2$ and PVA/LA/MgH$_2$ ratios have been carried out.

Influence of the monomer/PVA ratio on the melt-grown synthesis of copolymers

Reaction and yield in copolymers were strongly dependent on the ability of PVA to melt or dissolve in monomer to give a system with suitable viscosity. The monomer/PVA ratio equal to about 5 at least gave a limpid solution of PVA in monomer and high yield in graft copolymer (run 1,2,4–6 Table I and run 1–3,9,10 Table II). For CL/PVA and LA/PVA ratios smaller, system was not homogeneous enough and yield was lower (runs 3, 7–10 Table I and 4–8 Table II).

Conversion of CL and LA was followed for limpid solutions. Conversion rose to about 60% for 16 h

before the reaction mixture became very thick. The reactivity of LA was slightly higher than CL as shown by the representative curves for copolymerization of monomers in same conditions (Fig. 1). Since active species operating in CL and LA polymerization in this system should be structurally
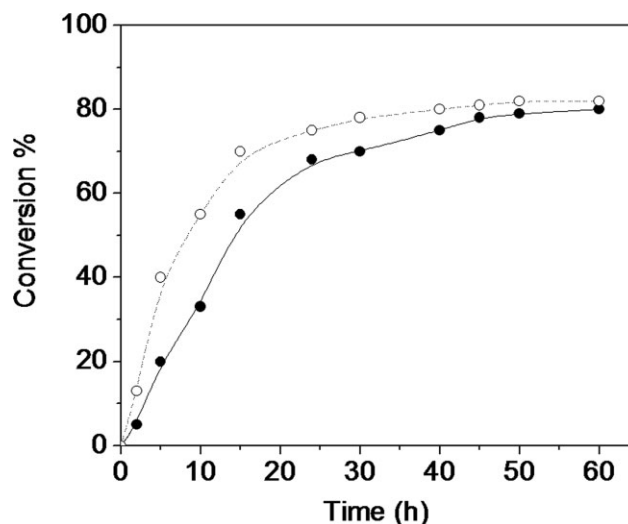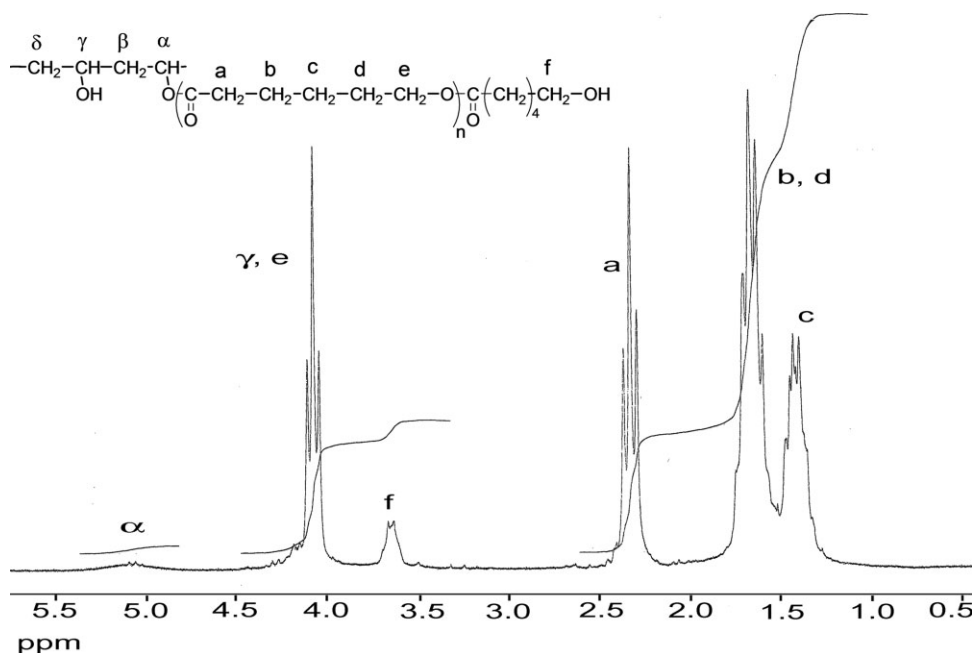

Figure 1 Conversion % of monomer *versus* time for the copolymerization of ε-CL with PVA (●) (run 5 in Table I) and L-LA with PVA (○) (run 3 in Table II). (no solvent, under argon, temperature 150°C).

Figure 2 ^{1}H-NMR spectrum (400 MHz) of PVA-*g*-PCL from melt-synthesis using MgH$_2$ as catalyst (25°C, solvent CDCl$_3$).

identical, the monomer reactivity seems to be related to the monomer ring size. The larger reactivity of 6-membered L-lactide than 7-membered ε-caprolactone was already shown for bulk homopolymerization.[25]

Yield could be slightly increased by maintaining heating cautiously to avoid partial degradation of PVA and copolymers leading to a browning of the mixture as detailed in experimental part. It is well known that PVA is sensitive to thermal degradation in molten and solid state which consisted of water elimination and chain scission via a 6-membered transition state leading to the formation of volatile products including saturated and unsaturated aldehydes and ketones.[26] A weight loss of 30% was recorded on PVA samples after 4 days at 180°C under argon.[27]

The addition of DMSO in the feed improved the limpidity of mixture at 150°C leading to good yield (runs 11–14 Table I and 11–14 Table II). However toxicity of solvent has not to be neglected because solvent was present at the time of synthesis and in copolymer as residues.

Spectrometric characterization of copolymers

PVA-*g*-PLA

The occurrence of grafting was shown by the appearance of the signal at 5.08 ppm in ^{1}H-NMR spectra due to the methine proton of the linkage between PVA backbone and PCL side chains (α in Fig. 2).[19,28] The methine proton of non-grafted PVA units (γ partially superimposed in Fig. 2) is situated at 4.14 ppm. The signals of the methylene protons of the PVA backbone (β, δ in Fig. 2) and those of the 3 methylene protons groups central to CL units of

PCL chains (b, c, d in Fig. 2) are situated between 1.2 and 1.8 ppm. The protons of methylene groups linked to carbonyl (a in Fig. 2) or oxygen (e in Fig. 2) of ester groups of PCL chains are shifted to 2.30 and 4.08 ppm respectively. Terminal methylene protons close to hydroxyl group of PCL chains (f in Fig. 2) is situated at 3.65 ppm.

Grafting was confirmed by ^{13}C-NMR mainly from the analysis of methine and methylene carbon signals of backbone chain. The formation of ester linkage resulted in small shift of methine carbon from 64.5 ppm for non-grafted to 66.3–68.3 ppm for grafted repeating units (γ and α in Fig. 3).[19,29] Methylene carbon near the ester linkage appeared at 42.5 ppm while the methylene carbon near the hydroxylated carbon group in non-grafted PVA units was located at 44.0–46.5 ppm (β and small broad peak δ in Fig. 3). Complete assignment was done in Figure 3.

Characteristics absorption bands in FTIR spectra were situated at 3444 cm^{-1} (ν$_{OH}$), 2947 cm^{-1}, 2866 cm^{-1} (ν$_{CH}$), 1727 cm^{-1} (ν$_{OC=O}$) and 1097 cm^{-1} (ν$_{C-OH}$) showing as evidence the presence of PVA and PCL chains.

PVA-*g*-PLA

As in precedent structure, grafting was clearly demonstrated in ^{1}H-NMR spectra by the presence of the methine proton of the ester linkage between PVA backbone and PLA side chains (α in Fig. 4). This signal at 5.40 ppm was assigned on the basis of analysis of related graft PVA spectra.[21,28,30] Following assignments were also done: methine proton of
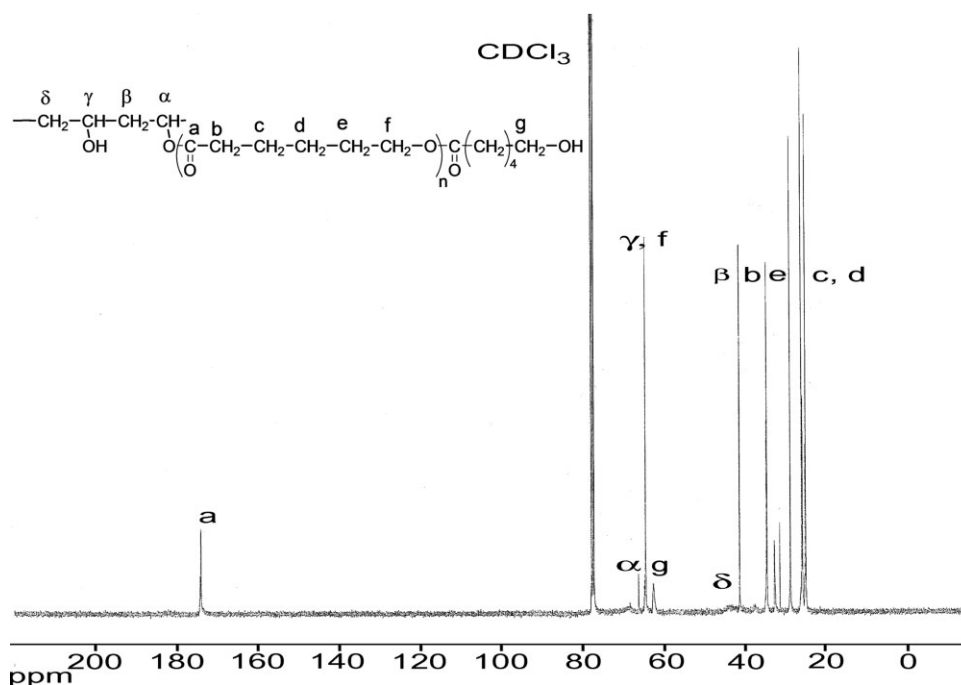
Figure 3 ^{13}C-NMR spectrum (100 MHz) of PVA-*g*-PCL from melt-synthesis using MgH$_2$ as catalyst (25°C, solvent CDCl$_3$).

non-grafted PVA units at 3.87 ppm (γ in Fig. 4), methylene protons of PVA backbone at 1.8–2 ppm (β, δ in Fig. 4), methine proton and methyl group of PLA repeating units at 5.16 ppm and 1.45 ppm (a,b in Fig. 4), methine proton and methyl group of end-PLA unit at 4.20 ppm and 1.30 ppm (c, d in Fig. 4).

In ^{13}C-NMR spectra, the connecting methine carbon on the PVA chain appeared at 69.42 ppm (α in Fig. 5). The carbon of the connecting ester group and the carbon of ester group in the PLA side chains appeared at 169.59 ppm and 175.08 ppm respectively (a in Fig. 5), methylene signal of PVA backbone (β, δ in Fig. 5) appeared at about 39 ppm with very weak intensity in excellent agreement with data reported.[21] Complete assignment was done in Figure 5.

FTIR spectra of the copolymers showed the main absorption bands at 3490 cm^{-1} (linked ν_{OH}) and 1761 cm^{-1} ($\nu_{OC=O}$).

Ability of MgH$_2$ to catalyse the reaction

Mixtures of PVA and CL or L-LA at 150°C for 48 h gave no detectable amount of copolymers showing that MgH$_2$ catalyst was essential to form PVA macro-initiator for ROP of monomers. Based on the following general reaction:

$$2\,\text{ROH} + \text{MgH}_2 \rightarrow \text{ROMgOR} + 2\text{H}_2$$
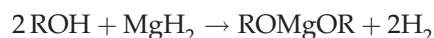
Mg divalent metal could lead to the possible formation of 2 simultaneous propagating species from 2

adjacent hydroxyl groups of PVA units forming a 6-membered ring[26] (scheme 1).

Such hypothesis suggested the eq. (3) to estimate the theoretical degree of substitution (DS$_{th}$) of PVA backbone. Comparison between theoretical and experimental degree DS$_{exp}$ [eqs. (1) and (5) from NMR] showed that DS$_{exp}$ was smaller than DS$_{th}$/2 for all runs (Tables I and II). Data allowed to conclude that only one propagating species on average, probably resulted from the reaction of MgH$_2$ and hydroxyl groups for steric bulk reasons.
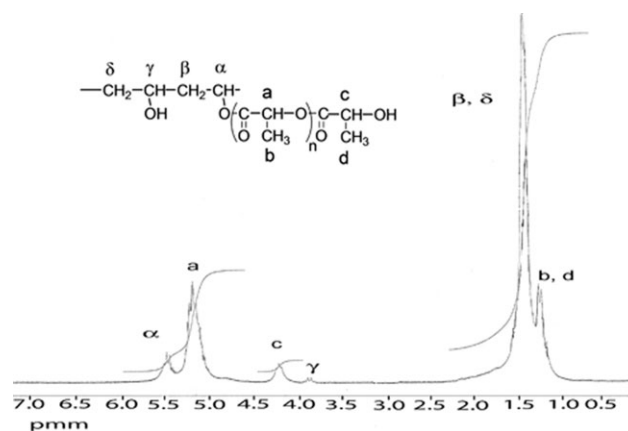
Figure 4 ^{1}H-NMR spectrum (400 MHz) of PVA-*g*-PLA from melt-synthesis using MgH$_2$ as catalyst (25°C, solvent CDCl$_3$).
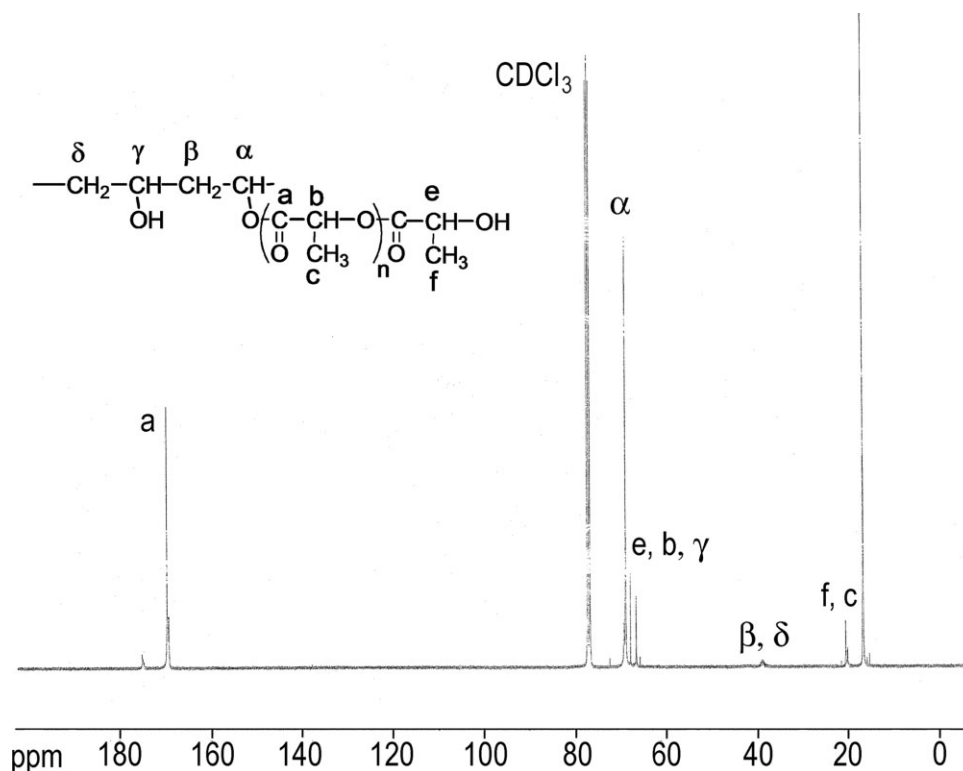
Figure 5 ^{13}C-NMR spectrum (100 MHz) of PVA-*g*-PLA from melt-synthesis using MgH$_2$ as catalyst (25°C, solvent CDCl$_3$).

Experimental degree of polymerization DP$_{exp}$ [eqs. (2) and (6)] was in a narrow range between 1 to 10, lower than DP$_{th}$ theoretical one [eqs. (4) and (7)].

M_n of PVA-*g*-PCL copolymers (runs 4–6 in Table I) were estimated [eq. (8)] from DP$_{exp}$ at 83,000, 143,000, and 148,000 g mol^{-1} while SEC in chloroform at ambient temperature with polystyrene standards, gave 68,000, 124,000, and 104,000 g mol^{-1} respectively. For PVA-*g*-PLA, M_n were estimated at 95,000, 112,000, and 117,000 g mol^{-1} (runs 7–9 in Table II) while SEC gave 65,000, 66,000, and 86,000 g mol^{-1}. No satisfactory correlation was noticed for copolymers from other runs in these experimental conditions. This originated partly in the limited solubility of copolymers and difference in swelling between PVA hydrophilic and PCL hydrophobic blocks.

DP$_{exp}$ is dependent on the monomer/MgH$_2$ ratio however it was not increased with high monomer contents (run 1, 2 in Table I and 1–5 in Table II) suggesting a limitation in chain growing during the propagation step.

A possible explanation for this is that besides intermolecular transesterification frequent in melt process, hydroxyl or alkoxide magnesium end groups of PCL and PLA chains cause backbiting via intramolecular transesterification leading to a DP$_{exp}$ decrease. Probably backbiting reactions are enhanced by large number of hydroxyl or alkoxy magnesium end groups and by the reaction temperature.[31,32]

Experimental degree of polymerization lower than theoretical one was also noticed for graft PVA copolymer synthesis in solution with Sn(Oct)$_2$ as catalyst showing the difficulties to control the polymerization totally.[19,21]

Thermal properties

Thermal properties of copolymers were determinate by DSC. For PVA-*g*-PCL only one glass transition temperature (T_g) and one melting temperature (T_m)
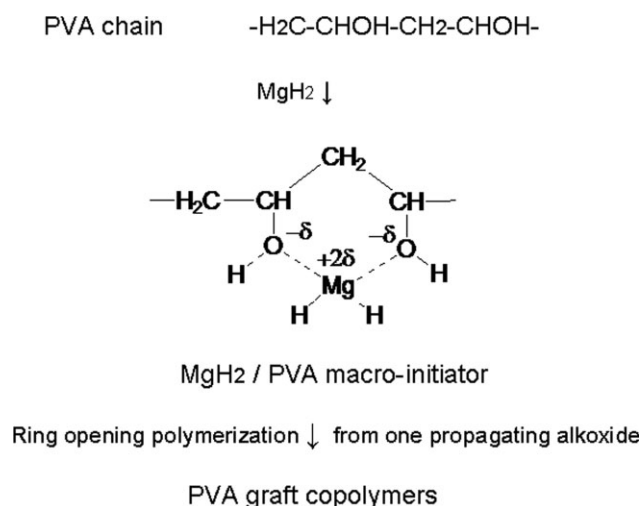
Scheme 1 Possible activated species.

TABLE III
Wettability and Surface Energy of PVA-g-PCL films and PVA-g-Polylactide Films

Polymer	Run (Table)	θ_{H_2O}[a] (°)	θ_{I2CH2}[a] (°)	γ_s^p [b] (mJ m^{-2})	γ_s^d [b] (mJ m^{-2})	γ_s [b] (mJ m^{-2})
PVA		54	55	29.1	23.2	52.3
PVA-g-PCL	4 (1)	57	37	15.9	34.2	50.1
	5 (1)	76	43	6.8	38.6	40.4
	6 (1)	78	41	5.1	35.7	40.8
PVA-g-PLA	2 (2)	66	43	12.0	32.4	44.4
	7 (2)	78	40	5.0	36.3	41.2
	8 (2)	81	46	4.5	33.4	37.9
	9 (2)	84	48	3.6	32.8	36.4

[a] Contact angle ($\pm 1°$) with water (θ_{H_2O}) and diodomethane (θ_{I2CH_2}).
[b] Surface energy ($\gamma_s \pm 1$ mJ m^{-2}), dispersive (γ_s^d) and polar (γ_s^p) components.

were observed. T_g was greater than T_g of PCL and lower than T_g of PVA ($-65°C$ and $68°C$ respectively) (Table I). T_g varied in about $30°C$ range and it decreased with increasing DP_{exp} and DS_{exp}. Decrease in T_g was in relation to the increase of free volume and mobility of copolymer chains resulting from the increase of the length and the number of PCL side chains. T_m was clearly observed for copolymers with highest DP_{exp} (run 1–6, Table I) because longer PCL side chains made easier possible organization in crystalline phase. Therefore, it can be assumed that PVA and polyester chains were miscible. For PVA-g-PLA, only one T_g was also observed but it was lower than T_g of PLA (about $57°C$). Moreover, broad melting peak areas were present on a wide temperature range about $60°C$ showing probable difficulties for the copolymer to crystallize in one phase (Table II). It seems that grafting PLA chains strongly restricted the crystallization of PVA backbone.

Amphiphilic properties of graft copolymers

Hydrophilic–hydrophobic properties of copolymers were evaluated by wettability and surface energy measurements on cast films from copolymer samples easily soluble in $HCCl_3$ or THF (Table III). A regular change of water contact angle θ_{H_2O} and surface energy γ_s from hydrophilic PVA film ($54°$ and 52.3 mJ m^{-1}) to PVA-g-PCL films ($78°$ and 40.8 mJ m^{-2}) and PVA-g-PLA films ($84°$ and 36.4 mJ m^{-2}) was noticed according to the amount of hydrophobic CL or LA monomer units grafted on the PVA backbone. The increase of θ_{H_2O} and the decrease of γ_s, mainly the decrease of γ_s^p polar component, according to the increase of DP_{exp}, DS_{exp} and PCL, PLA (Tables I and II) content, were indicative of the amphiphilic character of copolymers.

These θ_{H_2O} and γ_s optimal values are similar to those of PCL and PLA homopolymers showing that hydrophobic chains were oriented toward the surface of the films.

Hydrophilic–hydrophobic properties were also evaluated via the possible formation of micelle-like particles characterized by the CMC.

It can be in general assumed that for amphiphilic copolymers in a selective solvent below CMC, only molecularly dissolved copolymer, usually as unimers, is present in solution but above CMC multi-molecular micelles are in equilibrium with the unimers.

The report on PVA copolymers as a hydrophilic block for the formation of micelles in an aqueous phase is rare. In this domain, micelles from PVA randomly grafted with hydrophobic methacryloyl groups[33] and micelles from poly(vinyl alcohol-b-styrene) diblock copolymer were prepared by dialysis against water,[34] micelles from mixture of PVA with carboxy-ended polybutadiene were formed in aqueous solution by the precipitation method.[35]

From own experiment, it could be observed the formation of micelle-like particles in aqueous solution prepared from dilute solutions of PVA-g-PCL and PVA-g-PLA copolymers in THF followed by slow addition of water and slow evaporation of THF. CMC were measured at $25°C$ as the
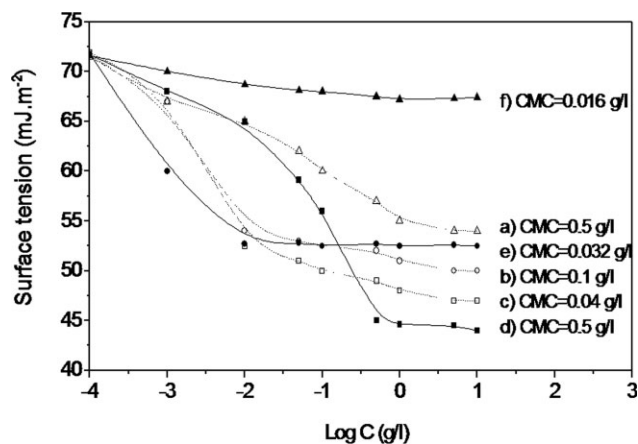

Figure 6 Surface tension of aqueous solutions of grafted copolymers versus concentration: PVA-g-PCL, a), b), c) respectively run 4, 5, 6 in Table I and PVA-g-PLA, d), e), f) respectively run 7, 8, 9 in Table II.

concentration corresponding with the change in slope of the curve of the surface tension of copolymer solutions in water versus the concentration.[36] CMC was in 0.5–0.02 g/L range and decreased according to the increase of PCL and PLA content (Tables I and II), DP_{exp} and DS_{exp} that is the length and the number of hydrophobic chains (Fig. 6). Micelle-like particles were stable with time up to about 10 g/L and resulted from a so-called closed association process based on amphiphilic properties. Higher concentrations led to the formation of viscous hydrogels that progressively and partially separated.

SUMMARY

The use of MgH_2 as catalyst for the formation of PVA macro-initiator for the ROP of CL and LA was established. One propagating alkoxide species resulted from the reaction of MgH_2 and hydroxyl groups of PVA backbone. The grafted copolymers were prepared in good yield in melt by adjustment of monomer/PVA ratio and temperature. PVA-*g*-PCL and PVA-*g*-PLA were characterized by ^{1}H- and ^{13}C-NMR, IR, SEC, DSC. Grafting of hydrophobic chains on hydrophilic PVA was demonstrated by the variation of wettability and surface energy as well as by the formation of micelle-like particles in aqueous solution. Interest for this method is the use of MgH_2 environmental catalyst, absence of solvent and possible recovery of solid material without further operation at the end of the polymerization process. Method could be expanded to other macro-initiators for the synthesis of copolymers to develop new materials particularly in medical sector.

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