ε-Caprolactone Grafting on a Poly(vinyl alcohol-*co*-vinyl acetate) in the Melt Without Added Initiator

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ABSTRACT: Polycaprolactone (PCL) grafting on vinyl alcohol-*co*-vinyl acetate) (PVA-Ac), was investigated in the melt at high temperature (170°C), below the PVA-Ac melting point, by ring opening polymerization of ε-caprolactone initiated by metal alkoxyde sites present in PVA-Ac: no additional initiator was used. The obtained average structures were determined by ^{1}H NMR. As expected, small grafts, with low average polymerization degree (DP), were obtained, between 4 and 12 h of reaction. These DP are due to exchange reactions between hydroxyl groups and PCL growing chains. The PVA-Ac was shown to be partially substituted by short PCL grafts. The DP linearly increased with the initial Lactone/PVA-Ac ratio, and the substituted alcohol sites rate were limited to 63%.It was shown that the used reactive system is characterized by a quazi-living polymerization mechanism. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2525–2531, 2007

Key words: PVA; ε-caprolactone; graft copolymers; anionic polymerization; living polymerization; NMR

INTRODUCTION

The modification of poly(vinyl alcohol-*co*-vinyl acetate) (PVA-Ac) by grafting small poly(ε-caprolactone) (PCL) chains is an interesting root for the preparation of new polyvinyl acetate (PVA) based biodegradable materials with tailored thermo mechanical properties.

PCL homopolymer are synthesized by ring opening polymerization of ε-caprolactone (CL) using various initiators or catalysts.[1]

Anionic ring opening polymerization of ε-caprolactone initiated by strong bases or organometallic compounds were frequently discussed: Na^+, K^+, Cs^+ metal alkoxide were used as active centers.[2] The mechanism of such polymerization involves the nucleophilic addition-elimination of the metal alkoxide on the carbonyl ester group. The propagating species are negatively charged and counter-balanced by the cation.

The anionic polymerization of lactones is known to be fast[3] leading to linear chains in the first steps of polymerization. Depending on temperature and reaction conditions back-biting reactions of the active chain ends can be obtained, randomly breaking down linear chains, and giving cyclic oligomers by-products.[2–5] The addition of protic compounds like alcohols to the reactive system leads to exchange reactions and a living-like character of the polymerization.[6–13] The used alcohols are either organic molecules with low molar masses or hydroxylated polymers. These alcohol functions can be located at chain ends or on the main backbone of natural or synthetic polymers.[14–18] When hydroxylated polymers are used, PCL functionalization results in important modifications of their original properties.

Polylactide[17] and PCL grafts[18] have been incorporated onto vinyl alcohol) between 100 and 130°C with Sn $(Oct)_2$ as initiator. The poly(vinyl alcohol) based graft copolymer having PCL side chains[18] were synthesized in DMSO, with DP of PCL varying from 4 to 23 and substitution degrees varying from 15 to 54%. With low DP, the copolymers were amorphous, while crystallinity from PCL was characterized at the highest incorporation rate.

The aim of this study is the preparation of a biodegradable copolymer using an ecologically friendly method: no additional catalyst and solvent should be used.

The used PVA-Ac was prepared by PVAc hydrolysis. After incomplete neutralization, some metal alkoxyde sites are present in PVA-Ac. In this study, it is intended to take advantage of the presence of these sites to initiate the ring opening polymeriza-

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TABLE I
Formulation for the Polymerization of the ε-Caprolactone (at 170°C)

PVA-Ac (g)	Run	ε-Caprolactone (g)	Reaction time (h)	CL/OHi (mole/mole)
400 (6.36 mole alcohol unit and 1.40 mole acetate unit)	1	155 (1.36)[a]	3	0.21
	2	232 (2.03)	3	0.32
	3	309 (2.71)	3	0.43
	4	386 (3.39)	3	0.53
	5	464 (4.07)	3	0.64
	6	541 (4.75)	4	0.75
	7	618 (5.42)	4.5	0.85
	8	781 (6.85)	5	1.08
158	9	842 (7.38)	24	2.94
123	10	877 (7.68)	26	3.92

[a] Values inside parentheses indicate ε-caprolactone in moles.

tion of ε-caprolactone leading to graft copolymers without addition of catalyst. Exchange reactions are expected to control the graft-length and minimize back biting reactions and cyclic oligomers formation.

Classically and without solvent, the PVA-Ac are dehydrated above their glass transition temperature. Strong intermolecular hydrogen bonds are obtained and the PVA-Ac behaves like a crosslinked polymer. Moreover, in the molten state and especially above 240°C, PVA-Ac is rapidly degraded.[19–21]

To avoid these undesirable reactions, caprolactone is expected to act as a reactive solvent: the reactive system should become a viscous liquid. The grafting reactions could thus be realized at relatively low temperatures (170°C).

EXPERIMENTAL SECTION

Materials

The PVA-Ac, commonly called PVA, was a KP 405 polyvinyl alcohol from Kuraray [mp = 191°C, T_g = 59°C measured by DSC at 10°C min^{-1} by two ramps from −60 to 200°C at 10°C min^{-1}, molar mass = 25,000 g mol^{-1} (Kuraray data)]. This PVA-Ac was prepared by partial hydrolysis of acetoxy groups of a poly(vinyl acetate). The hydrolysis rate was 82% as calculated from the ^1H NMR spectrum, in excellent agreement with the manufacturer data. The crystallinity was about 21% measured by DSC at 10°C min^{-1} (ΔH_∞ = 156 J g^{-1}) during the second ramp.

The used ε-caprolactone was supplied by Solvay, all the other reagents were purchased from Aldrich and were used as received.

Grafting reactions

The PCL grafting on PVA-Ac was made in a 2-L glass reactor (130 mm diameter) with a 3-necked steel cover. A steel anchor stirrer operating with a RW 28 W IKA motor at 40 rpm, a condenser and a T-type thermocouple probe were fixed to the cover. A nitrogen flow, previously dried in a silica column, allowed the air elimination from the reactor. The reactor was heated by an IKA HBR4 bath with silicon oil.

Process

The PVA-Ac was introduced in the reactor with a silicon oil bath temperature at 200°C. The lactone was first heated in a closed glass bottle at 120°C and introduced into the reactor 5 min after the PVA-Ac. The previous monomer heating reduces, from 40 to 20 min, the time necessary to obtain a homogeneous viscous aspect. For an initial mass ratio PVA-Ac/CL monomer of 400/464 a viscous blend is obtained around 150–155°C. When the reactive system became a homogeneous viscous liquid, the silicon oil bath temperature was decreased from 200 to 175°C. The reactants temperature stabilized at 170°C.

The reactive system was homogeneous in the macroscopic scale. This was confirmed by the NMR analysis of specimens taken at different points of the reactor during the reaction and at the end of reaction. Identical NMR spectra were obtained for all the analyzed specimens taken at identical reaction time.

Concerning the homogeneity at the microscopic scale, no evidence was found to affirm that the reactive system was homogeneous in the microscopic scale.

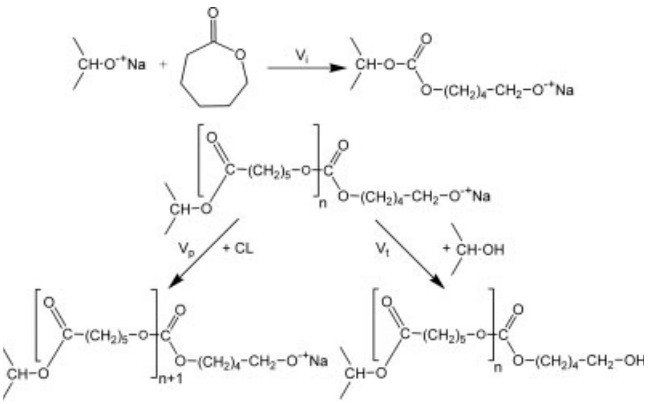
Characterizations

Thermal analysis

The thermal analyses were made with a Setaram DSC 141 under a nitrogen flow with a 10°C min^{-1} temperature ramp from −100 to 100°C.

NMR analysis

The NMR analysis analyses were performed with a Bruker DRX400 spectrometer operating at 400 MHz



Scheme 1 Synthesis of PVA-Ac/polycaprolactone copolymers by an anionic route.

for ^{1}H analysis and 100.3 MHz for ^{13}C analysis. The modified PVA-Ac was analyzed in DMSO-d_6 at 90°C. Chemical shift values (δ) are in ppm with reference to internal tetramethylsilane.

Charge measurements

The concentration of metal alkoxide functions in PVA was measured using a Mutek PCD-03 charge detector. A PVA aqueous solution (50 g PVA/L) was placed in the measuring cell; once the PCD-03 was turned on, a cell piston oscillates and causes a high flow rate. Any charged material adsorbed to the cell wall will be separated from its counterions by the flow and creates a steaming current. Two electrodes in the cell picks up this current and displays it on the unit. A polyelectrolyte of opposite charge is added until reaching the zero point of charge. The used PVA-Ac contained 232×10^{-6} cations/50 g.

Elementary analysis were realized at the center national d'analyze du CNRS at Solaise, France. The elementary analysis of the used PVA-Ac showed that it contains 41.7 μmol Na/g. This result is in good agreement with the charge detector result. This shows that alcoholates represents 0.26% of the total alcohols of the used PVA-Ac.

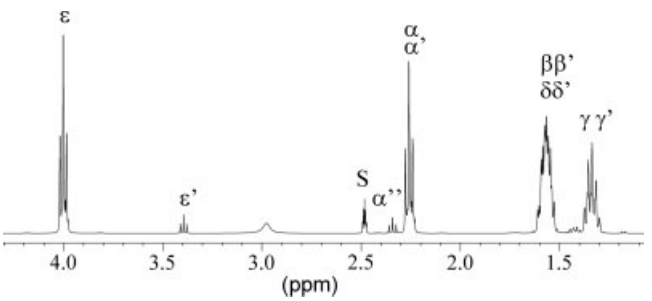


Figure 1 ^{1}H NMR spectrum of a poly-ε-caprolactone initiated by benzyl alcohol, acquisition in DMSO-d6, 90°C, (*S*: protonated residue of the solvent; protons of the benzyl group at low-field are not shown).[22]

RESULTS AND DISCUSSION

Polymerization without added catalyst

The diffusion of CL at high temperature (170°C) leaded to a viscous liquid blend. DSC analysis of specimens taken from PVA-Ac plates previously swelled by CL (up to 60 wt % CL) showed that a part of the crystalline phase remains infused at the reaction temperature (170°C). Nevertheless, the fact that the amorphous phase was dissolved in CL leaded to a viscous liquid allowing performing the reaction at 170°C. This considerably reduced the PVA-Ac degradation and also side reactions.

The used PVA-Ac was prepared by alkaline hydrolysis of a PVA. The analysis of this PVA-Ac (see Experimental Section) showed that some of the metal alkoxides sites remained in the polymer after neutralization: Alcoholates represents 0.26% of the total alcohols present in the PVA-Ac. These anionic sites could initiates a ring opening polymerization of ε-caprolactone.

The used PVA-Ac also contains alcohols, but are these functions enough nucleophilic to initiate the ε-caprolactone anionic polymerization? This was verified in a model study presented in the next paragraph.

We tried to realize the ε-caprolactone polymerization reactions in the presence of two secondary alcohols: Pentan-2,4-diol and 2,6-dimethyl-4-heptanol. No catalyst or initiator was added to the reactive system. After 4 h of reaction at 190°C, the reactive system was analyzed by NMR. No resonance were observed around 3.4 and 4 ppm, showing that the ε-caprolactone did not polymerize under these conditions

An ε-caprolactone polymerization reactions was realized using PVA-Ac at 170°C during 4 h. A PVA-Ac-*g*-PCL copolymer was obtained. (run 6, Table I).

This clearly shows that the alcohol functions present in the used PVA-Ac does not initiate CL polymerization and that the metal alkoxide present in the used PVA-Ac initiated ε-caprolactone ring opening polymerization.

In presence of alcohol functions, exchange reactions are obtained. These exchange reactions lower the polymer molecular weight. Such reactions are not only possible with the initially present alcohol groups and also with the newly formed PCL end chains.

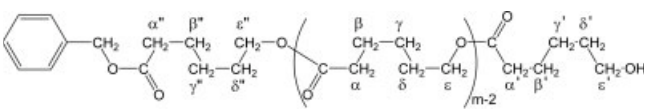


Figure 2 Poly-ε-caprolactone with DP = *m* initiated with triisobutylaluminum in presence of an important benzyl alcohol excess.

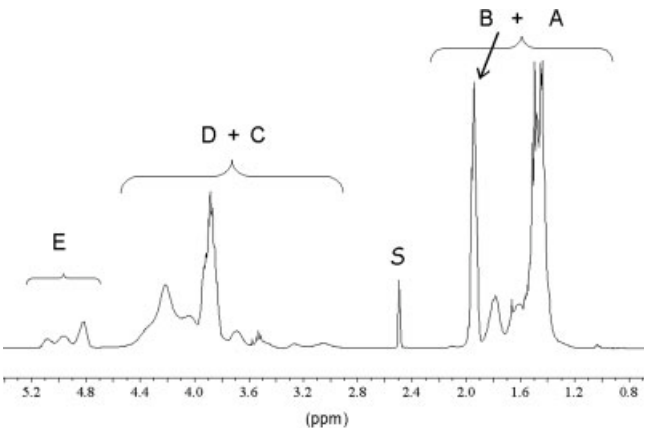


Figure 3 ^{1}H NMR spectrum of the PVA-Ac 405 in DMSO-d_6 at 90°C (*S*: protonated residue of solvent).

The principle reactions obtained are shown in Scheme 1.

PVA-Ac-*g*-PCL copolymers synthesis

Reactions were realized varying the PVA-Ac/CL ratio. the used formulations are presented in Table I.

The obtained products were analyzed by ^{1}H NMR. The presence or absence of caprolactone homopolymerization was first examined, than the substitution rate (SR) onto PVA-Ac hydroxyl sites and the average polymerization degree (DP) of PCL grafts were measured.

^{1}H NMR characterization of PCL

The ^{1}H NMR characterization of a PVA-Ac grafted PCL requires the previous study of a PCL spectrum in the same conditions (temperature and solvent). The Figure 1 shows the spectrum of a PCL supplied by Hamaide and coworkers[22] and prepared by anionic-coordinated polymerization in presence of benzyl alcohol and finally hydrolyzed and dried. Figures 1 and 2 presents the different PCL protons and their indexation on the ^{1}H NMR spectrum.

Since the ^{1}H NMR analysis allows to distinguish the ε′ methylene at the chain end (—C**H**$_2$—OH) from the (m − 1) other methylene (—C**H**$_2$—OCO—) noted ε and ε″, the DP can be readily calculated as follows from the (*A*) resonances areas,

$$\mathrm{DP} = A(\varepsilon + \varepsilon' + \varepsilon'')/A(\varepsilon') \quad (1)$$

Alternatively it can also be calculated by the ratio:

$$\mathrm{DP} = A(\alpha + \alpha' + \alpha'')/A(\varepsilon'). \quad (2)$$

^{1}H NMR characterization of the used PVA-Ac 405

As it is shown in the Figure 3, there are three well resolved resonance regions: (A+B), (C+D), and (E) available to characterize the PVA-Ac.

The Table II presents, from high to low-field, the attributions of the A, B, C, D, and E resonance regions of the ^{1}H NMR spectrum.

Structure of a vinyl alcohol modified by grafting of PCL

Three preliminary assumptions have been made: each PCL chain is grafted on the PAV-Ac chain onto an alcohol pendent group, each graft has a —CH_2OH end-group, and the number of acetate groups on the PVA backbone remain unchanged. It was shown that these assumptions were fully justified in the used experimental polymerization conditions because of a very low extent of both alcoholyse and transesterification side reactions except at high SRs (runs 9 and 10: Table IV). The latter cases will be discussed further.

The structure of such modified PVA-Ac is described in Figure 4, x, y, and z being respectively, the ratio of acetate units, unreacted alcohol units and grafted alcohol units. The sum ($x + y + z$) was normalized to 1 m is the average DP of lactone grafts. For the initial PVA-Ac: $x = 0.18$, $y = 0.82$, and $z = 0$.

Average DP

If it is considered that each PCL graft is terminated by an alcohol function, the average DP of the PCL chains is easily calculated from the ^{1}H NMR spectrum as previously indicated for the PCL homopolymer: [eqs. (1) and (2)]. But unfortunately, in the PVA-Ac-grafted-PCL copolymer, ε protons of the CL

TABLE II
Chemical Shifts and Attributions of PVA-Ac Protons

Domain	Proton		Resonance range (ppm)
A	Methylene	—CH_2—	1–2
B	Methyl of acetate	—O—CO—CH_3	1.9–2.0
C	Methine of alcohol unit	>CH—	2.8–4.6
D	Hydroxyl	—OH	4.2–4.6
E	Methine of acetate unit	>CH—	4.6–5.2

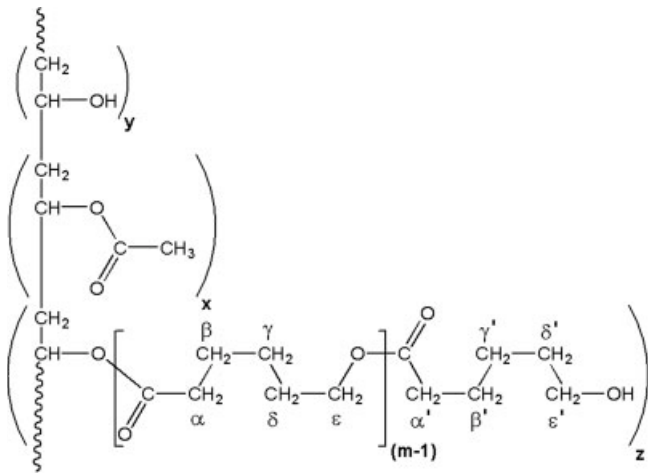


Figure 4 Structure of a PVA-Ac modified by the ε-CL.

units are overlapping with protons of PVA-Ac itself (Fig. 5 and Table III) and Eq. (1) gives overestimated DP values especially at low CL/OH formulations. This is attested by erroneous [A (ε) + A (ε′)] values higher than A (α +α′) values. So—in all cases—DP values were calculated using Eq. (2).

Fraction of the PVA-Ac alcohol functions bearing a PCL graft: SR

The SR was defined as the fraction of the PVA-Ac alcohol functions bearing a PCL graft.

To complete the grafted PVA-Ac description, it is necessary to determine the SR.

If each PCL chain end (ε′) corresponds to a substitution on the polymer backbone, then the substitution ratio (SR in %)—that is also a grafting efficiency—can also be calculated from the ^{1}H NMR spectrum since the attribution of all the spectrum resonances is easily realized (on the basis of those made previously for the PVA-Ac and the PCL). Finally, the >C**H**—O—CO—CH_2— resonances of the grafted structure (z) are expected in the same resonance zone as the >C**H**—O—CO—CH_3 (x) of the vinyl acetate units from PVA-Ac (Fig. 5, resonance region $S3$).

As shown in Figure 5 (left), three integration domains have been defined:

Domain 1 ($S1$): 0.8–2.4 ppm, Domain 2 ($S2$): 2.7–4.6 ppm, Domain 3 ($S3$): 4.7–5.2 ppm

The Table III presents the attributions of the different protons in the different domains.

The following system of equations derives from these attributions, where x, y, and z values can be calculated from the integrations ($S1$, $S2$, $S3$), the DP value of the PCL grafts being previously calculated m = A (α +α′)/A (ε′).

$$5X + 2Y + (8m + 2)Z = S1 \quad (3)$$

$$2Y + (2m + 1)Z = S2 \quad (4)$$

$$X + Z = S3 \quad (5)$$

The resolution of this system would allow the determination of the three unknown values x, y, and z ($x + y + z = 1$). In fact, the resolution of the system gives in many cases erroneous results: for example, the calculated Z value is not always compatible with Z obtained directly: $Z = A$ (ε′)/2 = $S6$/2, and $x = X/(X + Y + Z)$ value is sometimes found higher than its value $x_0 = 0.18$ in the initial PVA-Ac. This discrepancy is attributed to the presence of variable water protons in the $S2$ region and to resonances of residual caprolactone monomer in the high field part of $S1$ region (β′, γ′, and δ′ protons in the 1.1–1.7 ppm region). Besides, a direct determination of x ($x = S4/3$) must be excluded since it gives overestimated x values (higher than 0.18 found in the initial PVA-Ac) due to insufficient resolution of this resonance region particularly at high CL/PVA-Ac formulations.

Relying on previous assignments, but overcoming these problems since not using $S1$ area, a different

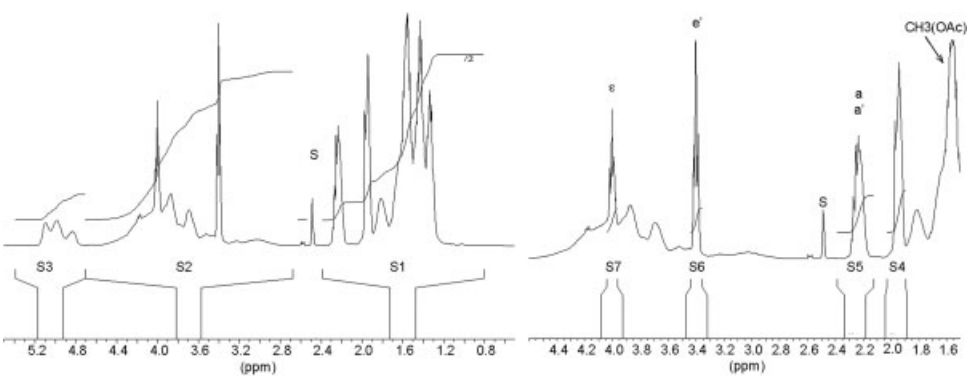


Figure 5 ^{1}H NMR spectrum of the PVA-Ac-g-PCL in DMSO-d_6 at 90°C: (left) $S1$–$S3$ integral, (right) $S4$–$S7$ integrals (S: protonated residue of solvent).

TABLE III
Resonances Attribution of the PVA-Ac Protons Modified by the ε-Caprolactone

Pattern	Proton		Domain	Number
Alcohol	Methine	>CH—	S2	Y
	Methylene	$-CH_2-$	S1	$2Y$
	Hydroxyl	—OH	S2	Y
Acetate	Methyl	$-O-CO-CH_3$	S1	$3X$
	Methine	>CH—	S3	X
	Methylene	$-CH_2-$	S1	$2X$
CL	Methine	>CH—	S3	Z
	Methylene	$-CH_2-$	S1	$2Z$
	ε ε′	$-CH_2-$	S2	2 (mZ)
	β β′ δ δ′ γ γ′ α α′	$-CH_2-$	S1	8 (mZ)
	Hydroxyl	—OH	S2	Z

and very simple determination of the complete structure (x, y, z, and m determination) is chosen :

$$\mathrm{DP} = m = S5/S6 \tag{6}$$

Z, X, and Y are given by the following expressions depending of $S3$ and $S6$ values (Fig. 5, right part)

The number of PCL grafts (CH—O groups) is equal to the number of CH_2—OH end groups: $Z = 0.5\ S6$.

The total number of >CH—O groups is $X + Z = S3$, then it holds $X = S3 - Z = S3 - 0.5\ S6$.

The acetate ratio is supposed to be constant $x = x_0 = (1 - y_0) = X/X + Y + Z$ and equal to 0.18, then the integral value $S3 = X + Z$ corresponds to a total number of units

$$Z + Y + X = \frac{(S3 - 0.5\ S6)}{x_0} \tag{7}$$

Then it holds

$$Y = \frac{(S3 - 0.5\ S6)}{x_0} - S3 = \frac{(y_0\ S3 - 0.5\ S6)}{x_0} \tag{8}$$

When expressed in ratios it holds:

$$X = X_0 \tag{9}$$

$$Z = \frac{0.5\ S6\ x_0}{S3 - 0.5\ S6} \tag{10}$$

$$y = \frac{y_0\ S3 - 0.5\ S6}{S3 - 0.5\ S6} \tag{11}$$

x_0 and y_0 are respectively, the fractions of acetate and alcohol units in the initial PVA-Ac (respectively, 0.18 and 0.82).

The molar ratio L_p/OHi (polymerized CL/initial alcohol functions) is calculated: $L_p/\mathrm{OHi} = zm/y_{0;}$ this value is generally lower than L_m/OHi value calculated from the initial formulation and shows that some monomer is lost by condensation on the vessel walls during the process. The true conversion rate (ρ) can be calculated. As for the very low residual monomer ratio (% L_m) remaining in the polymer, it is determined using the well resolved α protons at δ = 2.58 ppm. The ε protons are at 4.3 ppm ($S2$) and (β + γ + δ) at high field ($S1$), these regions being not used.

The SR of the hydroxyl functions by grafting, which is also a measure of the grafting efficiency is: $\mathrm{SR} = z/\mathrm{OHi} = z/y_0$.

Experimental results

Polymerizations have been realized with different initial PVA-Ac/L_m ratios. The reaction times have been adjusted—versus the formulation—to have an almost complete conversion ratio in all cases. This adjustment has been previously realized by NMR control on taken samples at different reaction times.

The results are presented in the Table IV.

The results (Table IV and Fig. 6) show that ring opening polymerization of the CL is obtained with-

TABLE IV
Structures of PVA-Ac-*g*-PCL Copolymers Calculated by ^{1}H NMR

Run	Lactone/ PVA-Ac (g/g)	Lm/OHi (mole/mole) (initial formulation)	Lp/OHi mz/OHi	ρ (%)	Residual Lm/Lm + Lp (%)	DP = m	Alcohol, Y	PCL grafts, Z	SR (%) z/OHi	Alcoholyse rate (%)
1	0.39	0.21	0.19	90	1.3	1.35	70.5	11.5	14	3.2
2	0.58	0.32	0.28	87.5	1	1.50	66.7	15.3	18.7	4.9
3	0.77	0.43	0.37	86	1.4	1.55	62.3	19.7	24	5.5
4	0.96	0.53	0.50	94.5	0.5	1.60	56.6	25.4	31	4.3
5	1.16	0.64	0.59	92	1	1.75	54.2	27.8	33.9	3.7
6	1.35	0.75	0.71	94.5	4	1.7	47.7	34.3	41.8	2.1
7	1.54	0.85	0.82	96.5	0.4	1.85	45.8	36.2	44.2	5.3
8	1.95	1.08	0.98	91	4.4	1.90	39.8	42.2	51.5	4.5
9	5.32	2.94	2.69	91.5	0.5	4.25	30.1	51.9	63.3	28.3
10	7.11	3.92	3.37	86	0.4	5.35	30.5	51.5	62.8	26.8

Synthesis in reactor without initiator at 170°C (values obtained without taking into account the side reactions).

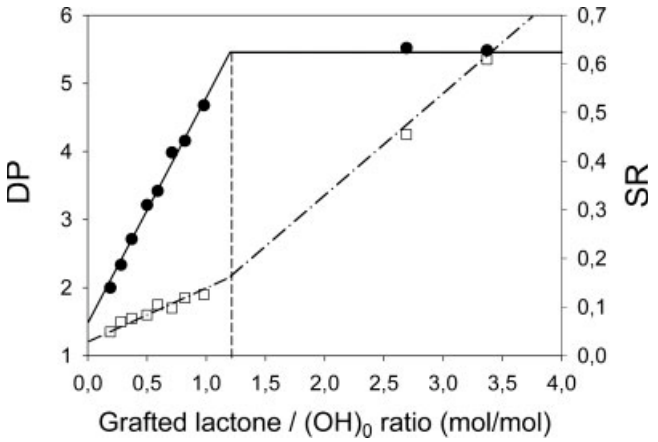


Figure 6 Polymerization degree [DP = $(\alpha + \alpha' + \alpha'')/\varepsilon'$] (□) and substitution rate of the hydroxyl groups (SR = $z/0.82$) (●) versus the ratio grafted CL units (L_p)/initial hydroxyl function $(OH)_0$ (mole/mole).

out any added initiator, initiation being very probably produced at 170°C by residual traces of bases used for the hydrolysis of the pendent acetate groups (traces of $CH3O^-Na^+$, or $>CH—O^-Na^+$ on the backbone).

It is important to note that for L_m/OHi initial molar ration increasing from 0.2 to 1.2, the DP and the SR increased linearly. The SR remained unchanged for L_m/OHi higher than one, while the molar mass of the PCL grafts increased. This shows clearly that for low values of L_m/OHi, exchange reactions to PVA alcohols groups are predominant. The exchange reactions to PCL alcohol end chains importance increased with the L_m/OHi and consequently with the SR. For L_m/OHi higher than 1.2, the SR remained unchanged (62%), while the molar mass of the PCL grafts increased showing that for these ratios, and when the maximum SR was obtained, the only exchange reaction that occurred were with PCL alcohol end chains showing clearly that the used reactive system is characterized by a quasi living polymerization mechanism.

CONCLUSIONS

An original functionalization of a PVA-Ac at 170°C by PCL chains grafting on alcohol sites in the molten state was presented in this study. Residual metal alkoxide sites coming from the PVAc (secondary metal alkoxide) alkaline hydrolysis initiated the CL ring opening polymerization. The used reactive system was characterized by a quasi living polymerization mechanism. Some of the PVA-Ac alcohol sites leaded to exchange reactions with PCL growing chains increasing the number of PCL grafts. Nevertheless the exchange reaction does not go to completion: Alcohol SRs lower than 63% were obtained.

In the next studies, microstructural analysis of the reactive system and obtained copolymers are expected to explain the observed reactivity of PVA-Ac alcohol sites and particularly correlate the alcohol trial configuration with the SRs.

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