Synthesis and Characterization of Poly(ethylene-*co*-vinyl alcohol)-*graft*-poly(ε-caprolactone)

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ABSTRACT: Graft poly(ε-caprolactone)s (PCLs) with high graft density were synthesized by using random copolymer poly(ethylene-*co*-vinyl alcohol) (EVOH) to initiate ring-opening polymerization of ε-caprolactone, with and without cocatalyst Sn(Oct)$_2$. The graft copolymer were characterized by IR, ^{1}H and ^{13}C NMR. The solution property and the crystallization behavior were also investigated.
    KEY WORDS   Poly(ε-caprolactone) (PCL) / Poly(ethylene-*co*-vinyl alcohol) (EVOH) / Graft Copolymer /

Poly(ε-caprolactone) (PCL) is a central important environmental friend and biocompatible polymer. It was synthesized through ring opening polymerization of ε-caprolactone (ε-CL) with various initiators or catalysts.[1,2] Recently, macromolecular engineering of PCL[3] was also developed in order to synthesize block, graft and hyperbranched (co)polymers.

Graft copolymerization of ε-CL can improve the mechanical properties of the homopolymers and the product can also be used as compatibilizer in polymer blends. There are generally two approaches to prepare graft copolymer of PCL. One of them is the macromonomer technique, in which PCL bearing a terminal double bond was synthesized beforehand. Using this approach, Jérôme and co-workers synthesized well-defined polystyrene-*g*-PCL,[4] poly(alkyl methacrylate)-*g*-PCL,[5] and poly(norbon-ene)-*g*-PCL[6] by controlled radical or organometallic catalyzed copolymerization of corresponding monomers and pre-made PCL macromonomers. The other approach is the "grafting form" technique in which the polymerization of ε-CL is (co)initiated by pendent hydroxyl group of a polymer backbone. For example, many natural polyhydroxy macromolecules such as starch,[7] dextran,[8] chitin,[9] and hydroxycellulose,[10] as well as synthetic polymers such as polyvinyl alcohol,[11] poly(ethylene-*co*-vinyl alcohol) (EVOH)[12] and functionalized polypropylene,[13] were grafted with PCL by ring opening polymerization from their pendent hydroxyl group. In addition, samarium-mediated graft polymerization of ε-CL on functionalized poly(*p*-xylylene)s was also achieved.[14]

In this paper, we report the synthesis and properties of a highly grafted copolymer, EVOH-*g*-PCL. The product is different from that in ref 12 in graft density because the hydroxyl content of EVOH in ref 12 ranges from 3.1 to 6.7 mol% and we use EVOH with much larger hydroxyl contents in this work. Therefore the graft density is so high that the copolymer exhibits special solution and crystallization properties. We will discuss these in details in the following. And the graft copolymer can lead to different end applications, for instance, hand-mouldable and degradable package.

EXPERIMENTAL

Materials

ε-Caprolactone (Aldrich, 99%) was distilled over calcium hydride under a reduced pressure before use. EVOHs (ethylene content 44 mol% and 27 mol%, Aldrich; ethylene content 32 mol%, Kuraray, Japan) were dried at 50°C *in vacuo* for 24 h. Stannous 2-ethylhexanoate (Aldrich, 95%) was used as received.

Polymerization

In a typical experiment, EVOH (1.0 g) was added to a well-dried schlenk flask under nitrogen atmosphere. Then ε-CL (10.3 g, 0.09 mol) and Stannous 2-ethylhexanoate (0.02 g, 4.9×10^{-5} mol) were injected into this flask. The reaction mixture was heated at 120°C for a predetermined period before cooled in an ice-water bath. After the viscous mixture being diluted by CHCl$_3$ (40.0 mL), the product was precipitated into a ten-fold excess of cold heptane. The collected polymer was washed with cold heptane and dried for 24 h at 25°C *in vacuo*.

Characterization

The molecular weight and the polydispersity index, $d = M_w/M_n$, were determined by gel permeation chromatography (GPC) using three Waters Styragel

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Table I. The graft copolymerization of ε-caprolactone at 120°C[a]

No.	Ethylene Content EVOH mol%	MI[e] of EVOH g 10 min⁻¹	Sn(Oct)$_2$ g	M_n[b] ×10⁴	D M_w/M_n	Conversion CL %	$[\eta]$ dL g⁻¹	T_m °C	ΔH_m J g⁻¹
1	44	3.5	0.020	12.3	2.30	58.9	0.48	38.2	49.8
2	32	1.3[c]	0.020	14.7	2.20	77.6	0.61	41.9	58.2
3	27	3.9	0.020	16.9	2.13	77.9	0.66	43.7	47.6
4[d]	27	3.9	0	8.3	3.48	40.0	0.41	–	–

[a]For all the polymerizations, Monomer/EVOH (g/g) = 10.3. [b]GPC in THF calibrated with PS standards. [c]190°C/2160 g. The condition of the others is 210°C, ASTM D 1238. [d]The reaction time is 30 h. The reaction time of the others is 20 h. [e] melting indices.

columns (pore size: 10^2, 10^3 and 10^4 Å in series), in THF at a flow rate of 1 mL min⁻¹ at 40°C. The elution time was detected by a Waters 410 RI detector. The columns were calibrated by narrow polystyrene standard. ^{1}H NMR measurement was carried out on a Bruker (500 MHz) NMR instrument using CDCl$_3$ as the solvent, and TMS as the standard. ^{13}C NMR measurement was carried out on a Bruker (300 MHz) NMR instrument.

Monomer conversions were obtained by thermogravimetric analysis (TGA) on a NETZSCH TG209 instrument on samples taken directly from the reaction. The temperature was elevated from 25°C to 550°C at a rate of 20 K min⁻¹ under the flow of nitrogen. The weight loss due to the evaporation of monomer takes place before 280°C, then a clear plateau appeared before the second weight loss from 310°C to 550°C due to the decomposition of polymer. Therefore, the weight loss above 300°C gives the polymer content, or conversion.

T_m and T_c were obtained on a NETZSCH DSC 204 instrument. In the first scan, the sample was heated from −10°C to 120°C at a rate of 5°C min⁻¹. Then the sample was cooled from 120 to −10°C at a rate of 10°C min⁻¹. The above procedure was repeated as the second scan.

RESULTS AND DISCUSSION

Polymerization of ε-CL Initiated by Hydroxyl Group on EVOH in the Presence and Absence of Cocatalyst, Sn(Oct)$_2$

The ring-opening polymerization of ε-CL was carried out in bulk in the presence of EVOH with and without Sn(Oct)$_2$. The mass ratios of ε-CL and EVOH were kept constant for all systems. The polymerizations were summarized in Table I. The products are all soluble in cold choloroform, while the graft copolymers in ref 12 containing less than 30–40 wt% are insoluble in cold choloroform. This is mainly due to the high
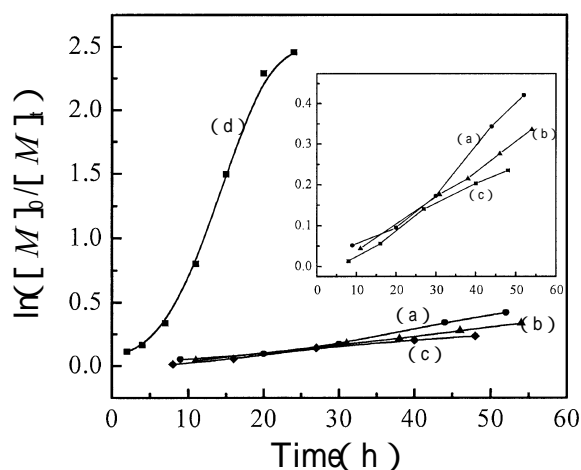

Figure 1. Kinetics of ε-CL polymerization in the presence of EVOH (a, b, c), and cocatalyzed with Sn(Oct)$_2$ (d). The ethylene contents of EVOH are 27% (a), 32% (b), 44% (c), 32% (d), respectively.

graft density copolymer synthesized in this work.

When the conversion is too high, the reaction mixtures become very viscous and eventually gelled. Therefore, the polymerizations were stopped just before the gelation takes place.

Figure 1 shows the kinetics of ε-CL polymerization in the presence of EVOH of different ethylene content, with and without Sn(Oct)$_2$. The polymerization rate for the system with Sn(Oct)$_2$ is much faster than that without cocatalyst. EVOH alone is able to initiate the polymerization, and therefore avoids introducing metal ion into the product, but it takes as long as 60 h to reach a moderate conversion. Figure 1 also shows that lower content of ethylene in EVOH (and thus higher content of hydroxyl group) causes a relatively faster overall polymerization rate.

Figure 2 shows the increase of M_n of the product along with monomer conversion for the systems without Sn(Oct)$_2$. The increase of M_n with conversion may be due to two reasons: the initiation of new chains by hydroxy group on the backbone of EVOH, and the propagation of the side chains.
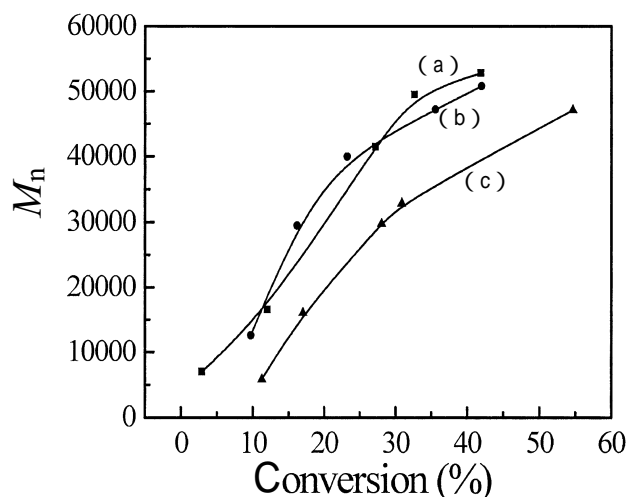
Figure 2. Dependence of molecular weight of EVOH-*g*-PCL on *ε*-CL conversion in the polymerizations without catalyst Sn(Oct)$_2$. The ethylene contents of EVOH are 44% (a), 32% (b), 27% (c), respectively.
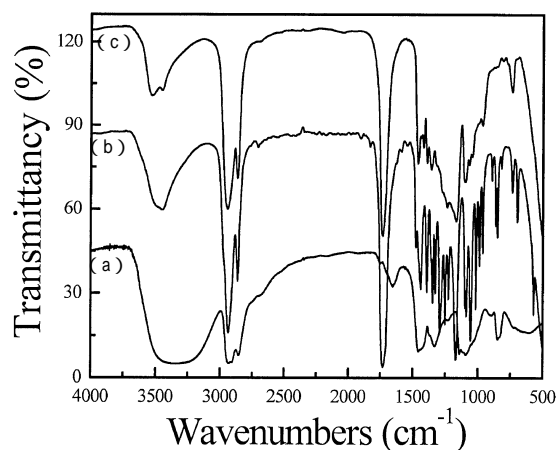

Figure 3. IR spectra of EVOH (a) and EVOH-*g*-PCLs at the polymerization time of 20 (b, **2** in Table I) and 30 h. (c). The polymerization was catalyzed by Sn(Oct)$_2$.

Characterization of EVOH-g-PCL

The formation of graft copolymer was supported by IR, ^{1}H and ^{13}C NMR of the resulting polymers. In IR spectrum (Figure 3), the absorption band of hydroxyl group at 3050–3550 cm^{-1} became a weaker and narrower peak because the hydroxyl groups were diluted in the resulting polymers. Meanwhile, a new peak at 1736 cm^{-1} appears which is assigned to ester carbonyl group coming from *ε*-CL skeleton.

A typical ^{1}H NMR spectrum of the graft copolymer was shown in Figure 4. Besides the main signals corresponding to protons on PCL and EVOH backbone, two small signals appeared at 4.96 and 3.65 ppm which are assigned to protons adjacent to chiral (H$_i$) carbons of EVOH, and methylene protons (H$_j$, –C*H*$_2$OH) in terminal group, respectively. The ratio of the integral areas below H$_i$ and H$_j$, 1 : 2, indicates that nearly all the ini-
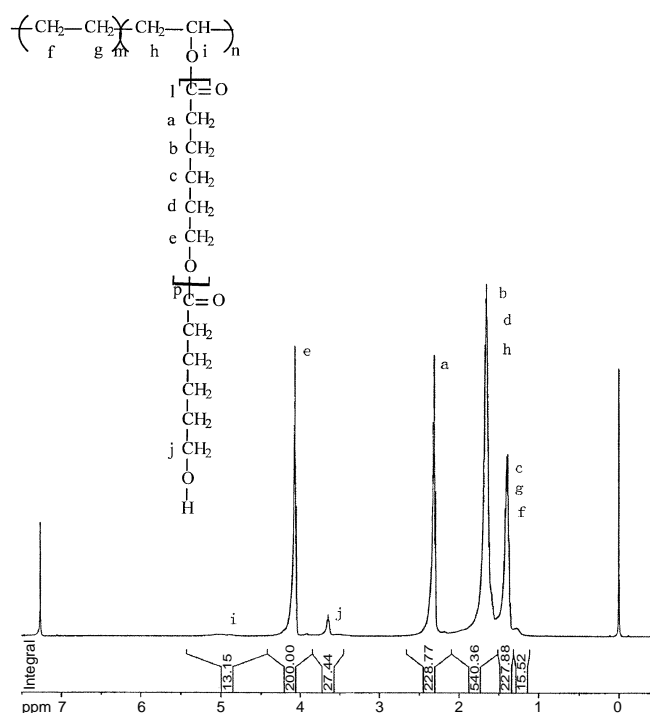
Figure 4. ^{1}H NMR of EVOH-*g*-PCLs at the polymerization time of 20 h (**2** in Table I).

tiating points in EVOH took part in initiation of *ε*-CL polymerization. The number average molecular weight of side chains is estimated as

$$M_{n,PCL} = 98^*(A_{He}/A_{Hj}) \approx 700 \text{ g mol}^{-1}.$$

According to the ratio of monomer/initiator = 10.3 g/g, we consider a polymerization using 1 g EVOH (ethylene content 32%) as initiator. The molar amount of hydroxy group in the initiator is calculated as 0.017 mol. Therefore, M_n of the side PCL chains is estimated as approximately 470 g mol^{-1} at 77.6% conversion, relatively close to that obtained from NMR measurement, 700 g mol^{-1}.

Taking into account the quite large M_n measured by GPC in Table I, we drew the conclusion that the product has a brush-like structure with many short PCL chains attached to an EVOH backbone.

The formation of graft copolymer was further confirmed by ^{13}C NMR spectrum shown in Figure 5. Besides all the typical signals due to PCL side chains, two additional signals are discernible at $\delta = 62$ and 31 ppm which are assigned to C$_i$ and C$_h$ in ethoxy unit of EVOH chain, respectively.

It is well known that the solution property of branched polymer is different from their linear analogues due to the more condensed globular structure. A common criterion for chain branching is Mark–Houwink value, α, which is always lower than a typical value for linear polymers, *ca.* 0.70.[15] We obtain molecular weight and viscosity for each GPC slice by
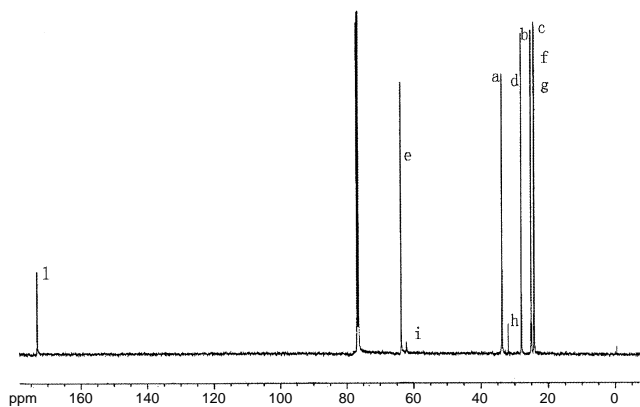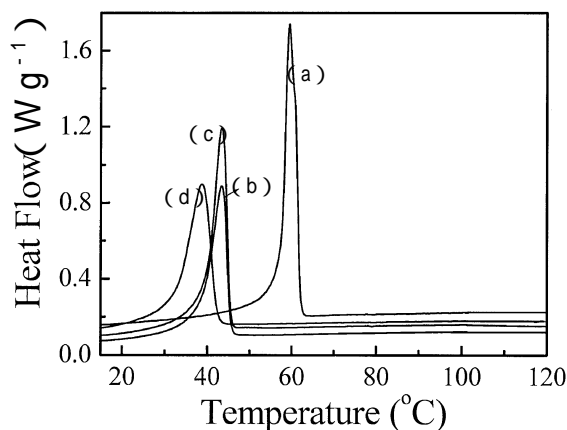
Figure 5. ^{13}C NMR of EVOH-*g*-PCLs at the polymerization time of 20 h (**2** in Table I).
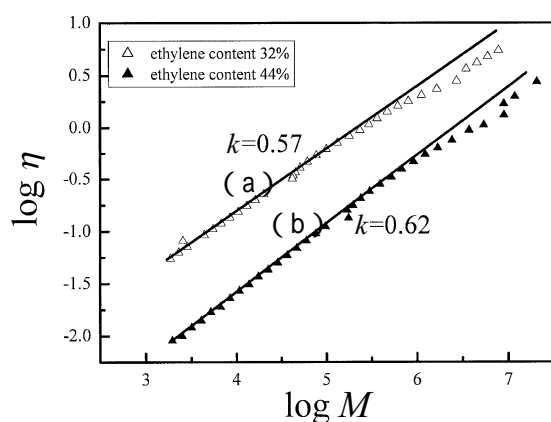
Figure 6. Double logarithm of intrinsic viscosity against molecular weight for EVOH-*g*-PCLs: **2** (a) and **1** (b) in Table I.

Figure 7. DSC curves of a linear PCL (a) and EVOH-*g*-PCLs: **3** (b), **2** (c), and **1** (d) in Table I.

an online LS and a viscosity detectors. Suppose each slice is nearly an equivalent to a narrow disperse fraction, we can get the value of α from the slope of double logarithm plot of viscosity against molecular weight. As shown in Figure 6, the values of α for graft polymers are 0.57 and 0.62, obviously lower than that of linear polymers. Furthermore, it seems that lower ethylene content (and thus higher hydroxyl content) leads to higher degree of branch because the α value is even lower.

Unexpectedly, the viscosity measurement (Table I and Figure 6) gave higher viscosity for more branched graft copolymer (from EVOH with higher hydroxyl content) than that for less branched, even at the same molecular weight. This might be due to the crosslinking through ester exchange reactions between different macromolecules during the polymerization. This side reaction is difficult to avoid because of the high polymerization temperature and the high conversion, although we tried to stop the reaction before macroscopic gelation. Nevertheless, the real reason is unclear with the current results and will be investigated in future work.

Melting Temperature Measured by DSC

PCL is a semi crystalline polymer. Differential scanning calorimetry (DSC) was utilized to investigate the melting temperature of linear homo-PCL ($M_w = 53000$) and graft copolymer. The former was synthesized by Sn(Oct)$_2$-catalyzed polymerization of ε-CL at 120°C. In the measurement, the sample was first heated from -10 to 120°C and then cooled to -10°C before second scan. Figure 7 shows the second scan. There is only one melting peak in the DSC curves. But in ref 12, there are two melting peaks, one attributable to the melting of PCL crystallites (at about 60°C), the second to PE crystallites (from 102 to 110°C), which means that PCL segments do not limit the crystallization capability of the PE segments.

The melting point of the graft copolymer is about 20°C lower than that of linear PCL in Figure 7. This could be due to the more complex architecture and the relatively low molecular weight of PCL side chains. Furthermore, there is a tendency that lower ethylene content of EVOH leads to a slightly higher melting point of the resulting polymer, possibly due to more ε-caprolactone grafted onto the main chain. Accordingly, the heat of fusion (ΔH_m) of the graft copolymer is smaller than that of homo-PCL (75.4 J g^{-1}), indicating lower crystallinity. This observation is in consistent with the results on polypropylene-*g*-PCL.[13] When the polymerization was conducted without Sn(Oct)$_2$, DSC did not result in any clear T_m data for the graft copolymers because of much shorter side chains.

The morphology of the graft copolymer by AFM (Figure 8) shows that, instead of spherulites formed in PCL homopolymer,[16] dendrite is more likely to form in graft copolymers when the thin EVOH-*g*-PCL film sample crystallized isothermally from the melt. This is a consequence of the more complex architecture in graft copolymer. The details are currently under inves-
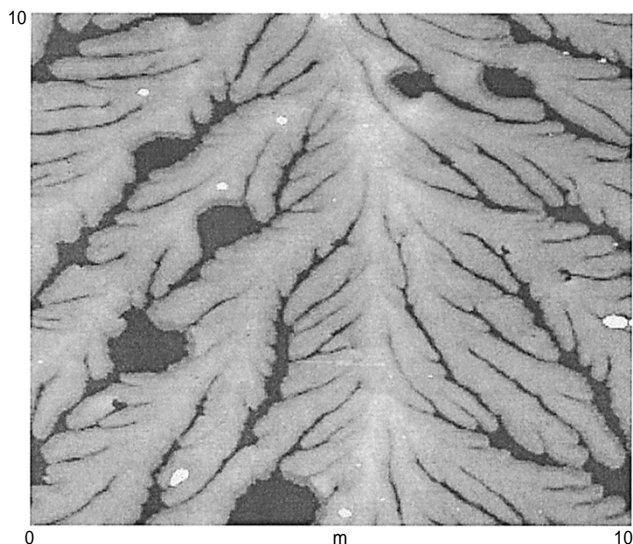
Figure 8. AFM image of an EVOH-*g*-PCL (**4** in Table I).

tigation.

CONCLUSION

The graft polymerizations of ε-caprolactone onto EVOH were achieved with and without $Sn(Oct)_2$. The resulting polymers have very high graft density, and therefore, exhibit special physical properties such as low Mark–Houwink values and low melting point. Thus a biodegradable PCL graft copolymer was synthesized with a melting point of about 40°C.

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