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Hybrid Copolymerization *via* the Combination of Proton Transfer and Ring-opening Polymerization

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Electronic Supplementary Information

Abstract Phosphazene base, *t*-BuP$_2$, was employed to catalyze the proton transfer polymerization (PTP) of 2-hydroxyethyl acrylate (HEA), and PTP was further combined with ring-opening polymerization (ROP) to exploit a new type of hybrid copolymerization. The studies on homopolymerization showed that *t*-BuP$_2$ was a particularly efficient catalyst for the polymerization of HEA at room temperature, giving an excellent monomer conversion. Throughout the polymerization, transesterification reactions were unavoidable, which increased the randomness in the structures of the resulting polymers. The studies on copolymerization showed that *t*-BuP$_2$ could simultaneously catalyze the hybrid copolymerization *via* the combination of PTP and ROP at 25 °C. During copolymerization, HEA not only provided hydroxyl groups to initiate the ROP of *ε*-caprolactone (CL) but also participated in the polymerization as a monomer for PTP. The copolymer composition was approximately equal to the feed ratio, demonstrating the possibility to adjust the polymeric structure by simply changing the monomer feed ratio. This copolymerization reaction provides a simple method for synthesizing degradable functional copolymers from commercially available materials. Hence, it is important not only in polymer chemistry but also in environmental and biomedical engineering.

Keywords Hybrid copolymerization; Proton transfer; Ring-opening polymerization; 2-Hydroxyethyl acrylate

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INTRODUCTION

Copolymerization is one of the most attractive methods for producing polymeric materials by which a variety of polymers with valuable functions have been synthesized from conventional, general-purpose monomers.[1−5] In general, copolymerization mainly occurs between monomers of the same type but with different structures through a single mechanism, such as radical,[6] ionic,[7] or ring-opening copolymerization.[8] However, although very difficult, it is also possible for different types of monomers to react simultaneously under the same conditions *via* different mechanisms. In fact, this type of copolymerization has been successfully realized and was named hybrid copolymerization.[9] Apparently, hybrid copolymerization remains a great challenge because of the significant differences between comonomers in both reactivity and nature of the propagating species.[9,10]

To the best of our knowledge, only a few types of hybrid copolymerization have been exploited. The first type refers to the hybrid copolymerization of zwitterionic comonomers such as 2-oxazoline and *β*-propiolactone.[11,12] During this polymerization, the reactions of ring-opening polymerization (ROP) and vinyl addition both occur. The second type is the radical ring-opening hybrid copolymerization of cyclohexenone acetal and vinyl monomers, which was first reported by Baily *et al*. in 1985.[13,14] One of the most attractive features of this method is that the resulting copolymers contain ether groups in the backbone, which imparts good degradability. The third type is the cationic hybrid copolymerization of vinyl ethers and oxiranes reported by Aoshima *et al*. in 2013.[15−19] This type of polymerization relies on a long-lived cationic propagating species. The last type is the anionic hybrid copolymerization of acrylate and lactone, which was first studied and utilized in marine antifouling by Zhang's group.[20−23] Very recently, we reported the anionic hybrid copolymerization *via* concurrent oxa-Michael addition and ring-opening polymerizations.[24] Due to the growing number of readily available comonomers, increasingly extensive research effort

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has been devoted to this field.

We herein wish to report a new type of hybrid copolymerization based on the ROP of lactone and the proton transfer polymerization (PTP) of 2-hydroxyethyl acrylate (HEA). The ROP of lactone is well known as a typical method for preparing aliphatic polyesters. In comparison, studies on PTP, which was reported in the 1950s by Matlack *et al.*,[25] are much scarcer. Different from the chain growth polymerization of vinyl monomers, which generally produces polymers with a C—C main chain linkage, the most attractive feature of PTP is that it can convert conventional vinyl monomers to aliphatic polyamides and polyesters by incorporating their functional groups into the polymer main chains.[26−31] Hybrid copolymerization combining the mechanisms of PTP and ROP would not only provide a simple method for the synthesis of degradable copolymers from commercially available materials but also offer a convenient functional structure designation.

EXPERIMENTAL

Materials

2-Hydroxyethyl acrylate (HEA) (>99.8%, from Shanghai Chemical Co., LTD.) was purified through an alumina column, distilled from calcium hydride (CaH_2), and stored under a nitrogen atmosphere. *ε*-Caprolactone (CL) (from Aldrich) was dried over CaH_2 and distilled under reduced pressure prior to use. Tetrahydrofuran (THF) (from Sinopharm) was freshly distilled from sodium/benzophenone and stored under an argon atmosphere. *t*-BuP_2 (2 $mol \cdot L^{-1}$ solution in THF) was used as received.

Polymerization

A typical procedure for the synthesis of HC-1 is described as follows. HEA (1.161 g, 10 mmol) and CL (4.566 g, 40 mmol) were charged into a round-bottom flask equipped with a magnetic stirrer. The flask was fitted with a septum. After three freeze-thaw-pump cycles, the flask was placed in an oil bath at 25 °C, and 250 μL of *t*-BuP_2 was injected to start the polymerization. The polymerization was quenched to room temperature and diluted with THF for analysis *via* GC and SEC. Finally, the polymer solution was precipitated into a large excess of cold *n*-hexane ethyl ether. The precipitate was filtered and dried in vacuo at room temperature, and analyzed by NMR spectroscopy.

Synthesis of a PHEA-*b*-PCL Block Copolymer

PHEA-*b*-PCL block copolymer was synthesized as follows. Purified PHEA (1.06 g, 5 mmol) and CL (0.23 g, 20 mmol) were charged into a round-bottom flask equipped with a magnetic stirrer. The flask was fitted with a septum. After three freeze-thaw-pump cycles, the flask was placed in an oil bath at 25 °C, and stannous octoate was injected to start the polymerization. The reaction was stopped by adding 1 mL of acetic acid. The crude product was diluted with THF, precipitated in diethyl ether, collected, and dried in vacuo.

Characterization

The molecular weight and polydispersity were obtained *via* size-exclusion chromatography (SEC) on an instrument equipped with a Waters 2414 differential refractive index (dRI) detector, a multiangle laser light scattering (LS) detector, and a Wyatt Visco Star viscometer detector (VD). HPLC-grade THF was used as the eluent at a flow rate of 1.0 $mL \cdot min^{-1}$. A series of narrowly dispersed polystyrene standards were used to calibrate the average molecular weight (M_w) and distribution ($Đ$). The structures of the polymers were analyzed using a Bruker ARX-500 NMR spectrometer at 25 °C with deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal standard. The monomer conversion was determined using an HP-689 gas chromatography (GC) instrument equipped with an HP-5 column (30 m × 0.54 mm × 0.5 μm); toluene was used as the internal standard. The carrier gas was hydrogen at 1 $mL \cdot min^{-1}$, and the column temperature was increased from a starting value of 60 °C at sample injection to a maximum of 300 °C at 10 $°C \cdot min^{-1}$.

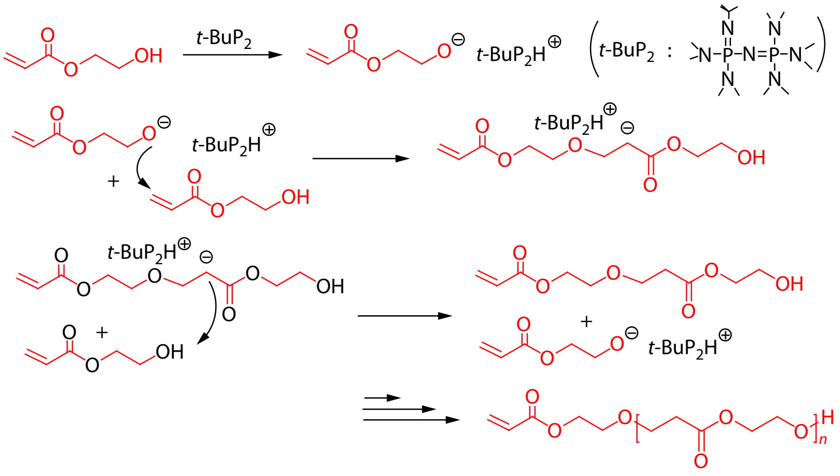
RESULTS AND DISCUSSION

Phosphazene Base Catalyzed PTP of HEA

Conventionally, the catalysts used for PTP are organometallic bases such as *t*-BuOK,[32] whose catalytic efficiency is quite limited. To overcome this drawback, PTP must be carried out at high temperatures, which might result in thermally induced vinyl addition reactions and crosslinking of the polymer. Phosphazene bases (PBs) are neutral Brönsted bases with extraordinary basicity and weak nucleophilicity.[33] These bases have an excellent solubility in organic solvents, and showed a very high efficiency in the anionic ROP of lactones or cyclic ethers at room temperature.[34−42] In view of these successful polymerizations, PBs were expected as effective catalysts for PTP. After a careful screening, *t*-BuP_2 with an intermediate basicity (pK_a = 33.5 in ACN) was chosen to catalyze the polymerizations. This is because in the coexistence of hydroxyl and acrylate groups, *t*-BuP_2 preferred to deprotonate the proton on the —OH group to form an oxygen anion, which could continue to react with acrylate following an oxa-Michael addition rather than a vinyl addition mechanism. These were confirmed by our previous report and Fig. S1 (in electronic supplementary information, ESI), where the *t*-BuP_2-catalyzed reaction of methyl acrylate (MA) and methanol (MeOH) only resulted in an oxa-Michael product.[43] Other PBs with a lower basicity than that of *t*-BuP_2 were without consideration due to their low efficiency for the ring-opening polymerization (ROP) of lactone, which is necessary for the hybrid copolymerization. The possible mechanism of the *t*-BuP_2-catalyzed PTP of HEA is shown in Scheme 1.

Polymerization study was initially performed in bulk at room temperature with [HEA]/[*t*-BuP_2] molar ratio at 20/1. As expected, the polymerization proceeded smoothly at room temperature, and the conversion of HEA reached over 95% as soon as the catalyst was added. Since PTP is a step-growth polymerization process, high yielding reactions are a prerequisite to obtaining high molecular weight polymers. Therefore, the polymerization was further performed for 24 h and finally afforded a polymer with a weight-average molecular weight (M_w) of 5.3×10^3 $g \cdot mol^{-1}$ and a molar mass distribution ($Đ$) of 2.30. Prolonging the reaction time to 48 h did not result in a further increase in the molecular weight.

To obtain more insight into the kinetics of polymerizations under these conditions, size-exclusion chromatography traces detected by refractive index detector (dRI-SEC) for the samples at different reaction time are shown in Fig. 1. The chromatogram at 1 min shows a broad polymer peak, which



Scheme 1 Possible mechanism of the *t*-BuP$_2$-catalyzed PTP of HEA.

gradually shifted to lower elution volumes with increasing reaction time, indicating an increase in the molecular weight of the polymer. Moreover, a peak at high elution volumes corresponding to oligomer was observed, which gradually weakened and completely disappeared at 1440 min (24 h). ^{1}H-NMR study on the kinetics (Fig. S2 in ESI) shows that almost all of the acrylate double bonds of HEA reacted at the polymerization time of 1 min. These studies confirmed the step-growth mechanism of *t*-BuP$_2$-catalyzed PTP.

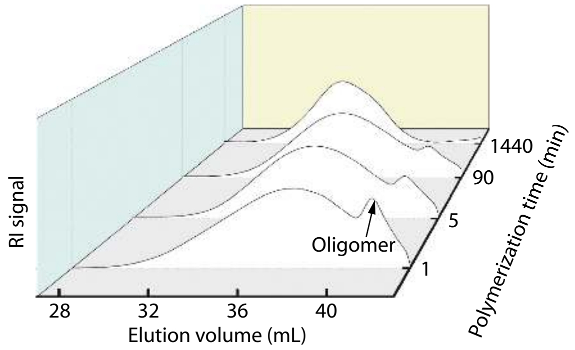


Fig. 1 dRI-SEC traces of samples taken at scheduled time intervals. [HEA]/[*t*-BuP$_2$] = 20/1.

^{1}H-NMR spectroscopy was employed to analyze the structure of the resulting polymer. The mechanistic scheme and the corresponding spectrum are shown in Fig. 2. The signals at 6.50−5.50 ppm are due to the double bonds. The signals at 3.84−3.70 and 2.56−2.48 ppm (proton 1′ and proton 2′) corresponding to the vinyl bond of HEA clearly show that polymerization proceeded according to the mechanism of PTP. The signals at 4.18−4.09 and 3.70−3.57 ppm (proton 3 and proton 4) are attributed to the ethane diol segments in HEA after PTP polymerization. The signals at 4.36−4.28 and 3.54−3.48 ppm (proton 5 and proton 6) are attributed to the methylene groups introduced *via* transesterification reactions (Fig. 2a). Hence, the proportion of transesterification (F_{trans}) can be calculated by the integration ratio of signal 6 to signal 2′ ($F_{\mathrm{trans}} = 1/2 \times S_6/S_2$). Here, the calculated value was 44.6%. Further detailed analysis of the ^{1}H-NMR spectra in Fig. 2 reveals that the signals corresponding to the terminal acrylic protons (1 and 2) are not obvious. Instead, a couple of signals can be clearly observed at 5.56−5.68 and 6.13−6.24 ppm. Similar signals were observed by Gibas *et al*., and they attributed them to the protons of pendant double bonds produced by the addition reaction between two acrylate vinyl groups.[44] However, it is very difficult for the proton of an acrylate vinyl group to be abstracted by *t*-BuP$_2$. Hence, more suitable explanation is still expected.

The structure of the polymer can be further confirmed by the MALDI-TOF MS spectra in Fig. 3. As shown in Fig. 3(b), the signals due to the PTP (A) and transesterification reactions (C and D) can be clearly observed. A similar structure was reported for the N-heterocyclic carbenes-catalyzed polymerization of HEA.[29] Besides, signal B can be attributed to the oxa-Michael addition reaction between the terminal vinyl group of the polymer and the trace amount of H$_2$O.

After confirming the polymer structure, a variety of reaction conditions were evaluated, and the results are summarized in Table 1. Raising the temperature from −30 °C to 25 °C increased the M_{w} value from 3.6×10^3 g·mol^{-1} to 5.3×10^3 g·mol^{-1}; furthermore, $Đ$ increased from 1.68 to 2.30 (PHEA-2 to PHEA-4). Unexpectedly, with a further increase in temperature, this value decreased (PHEA-5). This might be due to the formation of microgel, which could be removed before SEC analysis. This hypothesis was further proven by the results of polymerization at 100 °C, in which obvious gelation was observed (PHEA-6). The gelation reaction was caused by the thermally initiated vinyl reactions, and the vinyl species could be produced either by the transesterification reaction between HEA monomer and oligomers in Fig. 2 or by the addition reaction. Increasing the molar ratio of HEA to *t*-BuP$_2$ from 10/1 to 40/1 (PHEA-7), M_{w} of the resulting polymers increased. Further increasing the molar ratio (PHEA-7) only resulted in a slight increment in M_{w} (PHEA-8) despite that all the polymerizations reached a very high monomer conversion (> 98%). This is because the PTP of HEA proceeded through a step-growth polymerization mechanism, where the molecular weight of the resulting polymer is mainly determined by the fraction of functional groups rather than the ratio of monomer to catalyst.

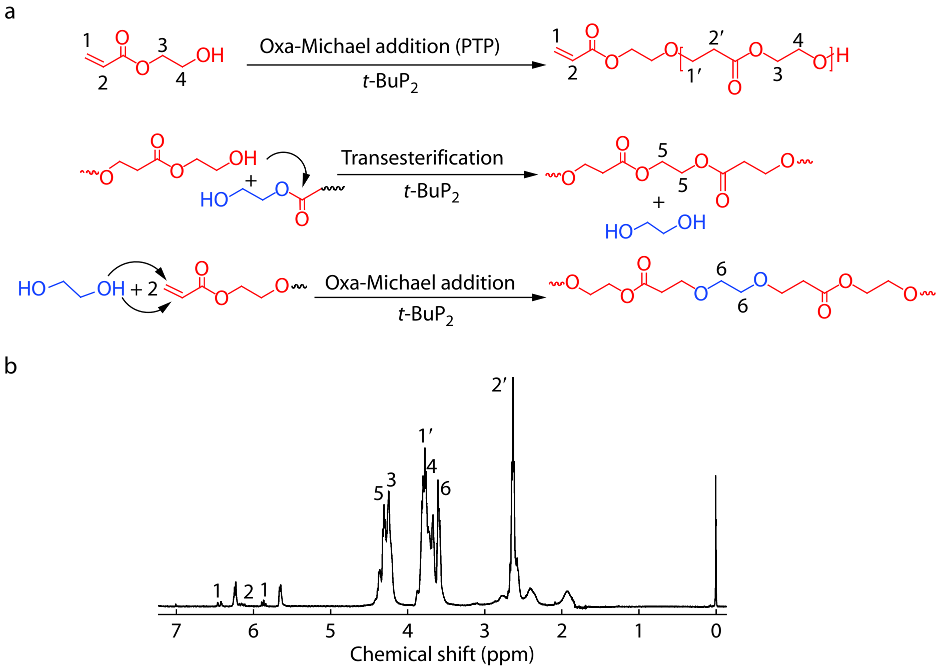


Fig. 2 (a) Mechanistic scheme and (b) ^{1}H-NMR spectrum of the corresponding product after careful purification. [HEA]/[t-BuP$_2$] molar ratio is 20/1, room temperature. The sample was quenched by a benzoic acid solution in ethyl alcohol (EA).

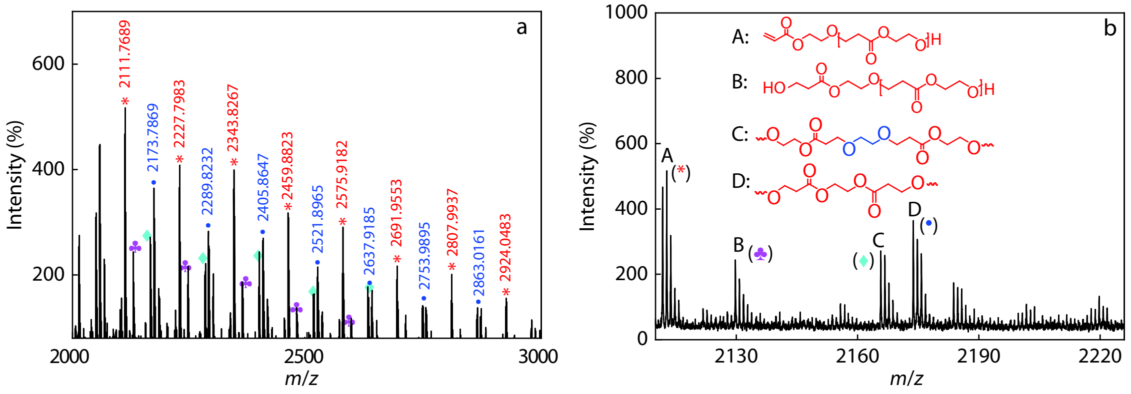


Fig. 3 (a) Full MALDI-TOF MS spectrum and (b) magnified area of the corresponding product for PTP of HEA. [HEA]/[t-BuP$_2$] molar ratio is 20/1.

Table 1 Overview of the reaction conditions evaluated for the t-BuP$_2$-catalyzed PTP of HEA and the resulting SEC weight-average molecular weight and distribution.

Sample	HEA/t-BuP$_2$	Temperature (°C)	Time (h)	Conv.$_{\text{HEA}}$ (%)	$M_w \times 10^{-3}$ (g·mol^{-1})	$Đ$
PHEA-1	10/1	25	24	99.7	2.00	1.56
PHEA-2	20/1	−30	24	98.5	3.60	1.68
PHEA-3	20/1	0	24	98.6	4.06	1.87
PHEA-4	20/1	25	24	99.1	5.30	2.30
PHEA-5	20/1	60	24	100	2.16	2.46
PHEA-6	20/1	100	24	Gel		
PHEA-7	40/1	25	24	100	6.21	2.63
PHEA-8	100/1	25	24	100	6.89	2.89
PHEMA-1 [a]	20/1	25	24	<5		

[a] The monomer employed was 2-hydroxyethyl methacrylate (HEMA).

Moreover, the enzymatic degradation for the resulting polymer was also studied. As shown in Fig. S3 (in ESI), the significant decrease in molecular weight for the polymer suggests a good degradability of PHEA-5. In addition, we also tried the t-BuP$_2$-catalyzed PTP of hydroxyethyl methylacrylate (HEMA) under the similar condition. However, only very low monomer conversion was observed, which might be due to the steric effects of methyl group.[44] Anyhow, the before-mentioned results confirmed that *t*-BuP$_2$ was an effective catalyst for the PTP of HEA.

Hybrid Copolymerization of HEA and CL

In general, the mechanism of PTP is believed to involve Michael addition polymerization by the attack of alkoxide anions on the acrylate double bonds. It is well known that *t*-BuP$_2$ can also effectively catalyze the ROP of lactone, which also involves an alkoxide ion. Inspired by these results, we sought to combine PTP and ROP and perform a crossover between the two polymerization reactions simultaneously. According to the above study on the PTP of HEA, a transesterification reaction was also expected to occur during polymerization.

We first examined the copolymerization of ε-caprolactone (CL) and HEA with a [HEA]/[CL]/[*t*-BuP$_2$] molar ratio of 20/80/1 at 25 °C. Two polymers and corresponding mechanisms were possible. In the first and simplest case, the resulting polymer is an acrylate terminal polyester, similar to the polymer from the stannous 2-ethyl hexanoate-catalyzed ROP reported by several groups.[45] During the polymerization, the acrylate double bond of HEA does not take part in polymerization, and HEA acts as only an initiator. However, this case would produce minimal polymer with high molecular weight due to the limited molar ratio of monomer to initiator. The second and more expected possibility is that HEA works as a monomer for PTP and meanwhile gives an alkoxide anion for the ROP of ε-CL. This dual function would result in a polymer with an ester-ether structure in the main chain.

Fig. 4(a) shows the predicted structure of the product (HC-1 in Table 2), and Fig. 4(b) shows the corresponding ^{1}H-NMR spectrum with the signals assigned. The characteristic signals of the CL and HEA units are clearly observed in the ^{1}H-NMR spectrum, suggesting that both monomers participated in the polymerization. Moreover, signals 1 and 4 corresponding to the ether structure further demonstrate that HEA took part in the polymerization according to the PTP mechanism but not vinyl addition. Comparison of the intensities of the signals at 1.48−1.30 ppm corresponding to CL and those at 2.68−2.50 ppm (proton 2) corresponding to HEA shows that the fraction ratio of CL units to HEA in the copolymer was 4.93, which is slightly larger than the feed ratio of 4.00 (Table 2). More importantly, a new signal for proton 12 corresponding to the CL-HEA diad is clearly observed at 3.47–3.37 ppm. The other new signal for proton 13 corresponding to the alternate HEA-CL diad should appear at 4.28–4.25 ppm. Unfortunately, this signal overlapped with that of proton 5 resulting from the transesterification which is also observed at the PTP of HEA in Fig. 2. As the cases of PTP of HEA, signals corresponding to the terminal acrylic protons were found at 5.81–5.92, 6.06–6.24, and 6.32–6.45 ppm, suggesting that this polymer can be used as a macromonomer. The dRI-SEC trace in Fig. 4(c) shows a high M_w (1.26 × 10^4 g·mol^{-1}) and a narrow distribution (1.42). Together, all of these results suggest that the resulting product had an ester-ether copolymeric structure and prove that the polymerization proceeded by combining ROP and PTP. Moreover, a block copolymer (HC-7, in Table 2 and Fig. S4 in ESI) was specially prepared by using the purified homo-polymer of HEA (PHEA-2 in Table 1) to initiate the ROP of CL, which was catalyzed by stannous octoate. As predicted, the NMR spectrum for the block copolymer HC-7 in Fig. 5 clearly shows the disappearance of the signal 12. Furthermore, due to the absence of alternate HEA-CL diad (signal 13), the integration of signal 5 is much smaller than that of

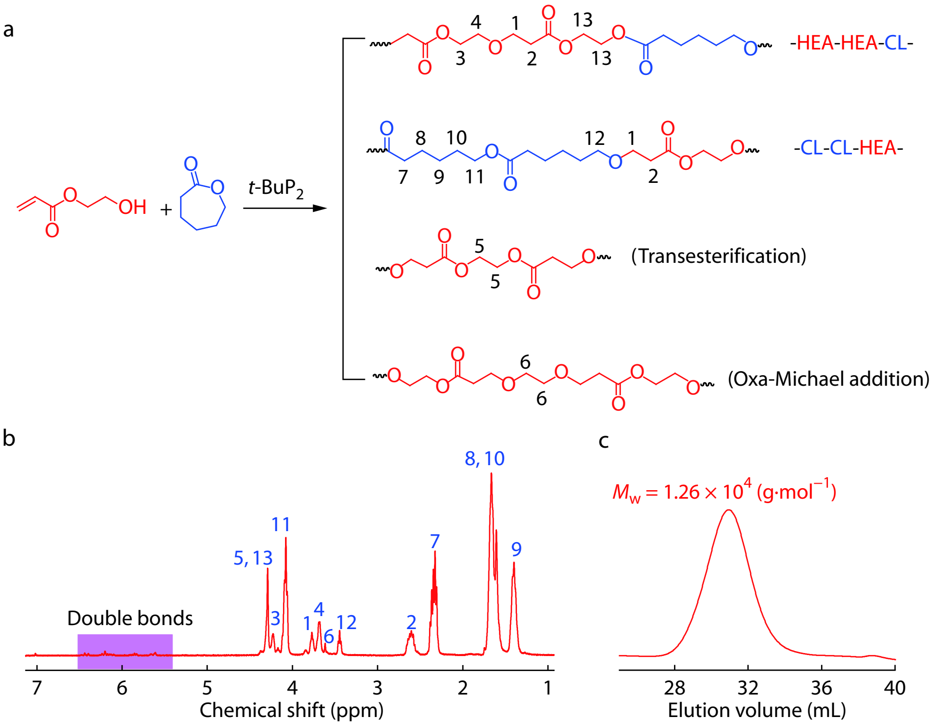


Fig. 4 (a) Predicted synthetic scheme, (b) ^{1}H-NMR spectrum, and (c) dRI-SEC curve of the resulting copolymer HC-1.

Table 2 Hybrid copolymerization *via* a combination of ROP and PTP.

Sample	HEA/CL/*t*-BuP$_2$	Temperature (°C)	Time (h)	Conv.$_{HEA}$ (%)	Conv.$_{CL}$ (%)	$M_w \times 10^{-4}$ (g·mol^{-1})	$Đ$	F_{HEA} (%)
HC-1	20/80/1	25	6	99.9	100	1.26	1.42	20.1
HC-2	20/80/1	60	6	99.9	99.9	3.13	4.39	20.3
HC-3	20/80/1	60	32	99.9	99.9	Gel		
HC-4	10/90/1	25	6	99.2	99.3	1.38	1.45	12.2
HC-5	50/50/1	25	6	98.7	100	0.79	2.62	48.5
HC-6	90/10/1	25	6	99.5	99.9	0.22	2.95	89.8
HC-7 [a]	20/80/1	25	6	99.5	99.9	3.64	4.26	19.8

[a] Block copolymer synthesized by two-step method.

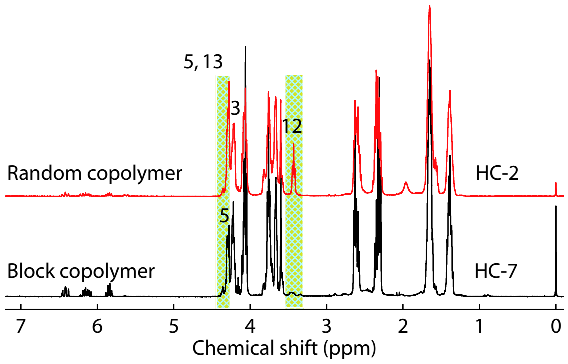


Fig. 5 ^{1}H-NMR spectra of HC-2 and HC-7. HC-7 was a block copolymer synthesized by a two-step method.

the corresponding signal for the random copolymer HC-2. These ^{1}H-NMR spectra provide a solid proof for the random copolymer and the hybrid mechanism for the copolymerization of HEA and CL.

More evidence was obtained by ^{1}H-^{13}C HMBC NMR spectroscopy and MALDI-TOF mass analysis. Fig. 6 presents the ^{1}H-^{13}C HMBC NMR spectrum of HC-1. Proton 2 is related to those on carbon atoms 1, 8, 9, 10, and 12, which correspond to carbon atoms in the CL and HEA units. This result confirmed the presence of an alternate CL-HEA diad. MALDI-TOF MS was also employed to analyze the resulting polymer. As shown in Fig. 7, two major populations are found in the MALDI-TOF mass spectrum. The deviation between these two close signals is 60, which is equal to the molar mass of an —OCH$_2$CH$_2$O— group, indicating that one of the populations resulted from transesterification and oxa-Michael addition reactions. Regardlessly, the alternate diads are clearly found for each polymer, confirming again the copolymeric structure. The thermal and hydrophilic properties of the synthesized copolymer were also studied by DSC and contact angle. As shown in Fig. S5 (in ESI), the melting temperature (T_m) and the degree of crystallinity of PCL were 56.2 °C and 60.8%, respectively. For the copolymer, despite that the exothermic crystallization peak did not completely disappear, it shifted to 32.4 °C, and the degree of crystallinity decreased to 50.1%. These phenomena occurred because the existence of a copolymeric structure destroyed the molecular chain regularity and hence prevented crystallization of the polymer. In addition, a large number of ether groups were incorporated into the polymer chains, which made the resulting polymer more hydrophilic. Hence, the water contact angle of the resulting copolymer was smaller than that of PCL. Note that both

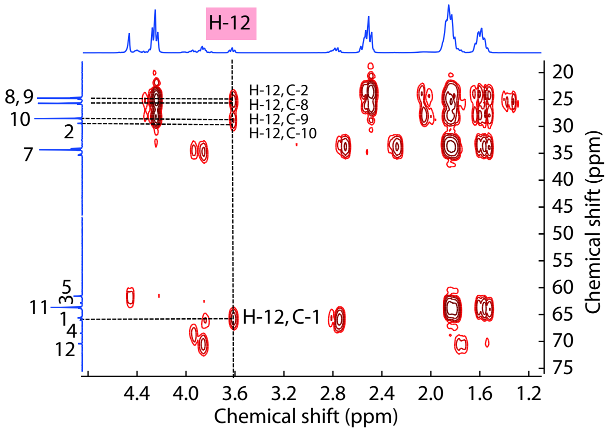


Fig. 6 ^{1}H-^{13}C HMBC NMR spectrum of copolymer HC-1 synthesized with a [HEA]/[CL]/[*t*-BuP$_2$] molar ratio of 20/80/1 at 25 °C.

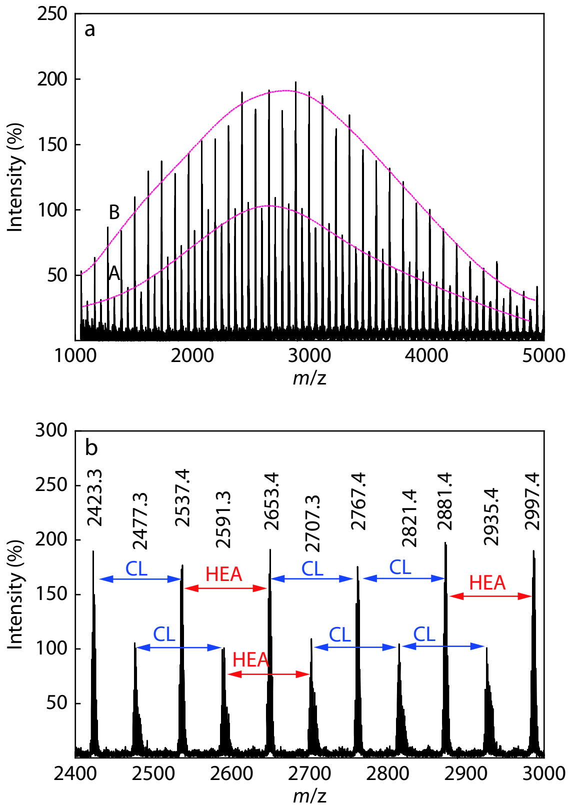


Fig. 7 (a) Full MALDI-TOF MS spectrum and (b) magnified area of copolymer HC-1.

the decrease in crystallinity and the increase in hydrophilicity help to accelerate degradation.

Next, we studied the polymerization process by removing aliquots of the reaction mixture at predetermined time for ^{1}H-NMR characterization. Typical examples at 0 (before *t*-BuP$_2$ was added), 1, and 10 min are given in Fig. 8(a). As shown, the intensity of the signals at δ = 5.80–6.61 ppm assigned to the acrylic protons of HEA dramatically decreased within 1 min, suggesting that both monomers were rapidly consumed. Comparison of the intensities of the corresponding signals indicated that the conversion of CL and HEA reached 99.8% and 74.6%, respectively, when the polymerization proceeded for 1 min. For a longer polymerization time of 10 min, 100% CL and 82.1% HEA were converted into polymer. The SEC traces in Fig. 8(b) show that the peaks of molecular weight of the aliquot withdrawn at 1 min were observed at approximately 38–40 mL, one of which disappeared at 10 min, suggesting that the oligomers were continually converted into polymer of high molecular weight (6730 g·mol^{-1}). This value shifted slightly to 7569 g·mol^{-1} at 10 min. Meanwhile, two small peaks correspond to the oligomers.

We then conducted further experiments to investigate the influences of reaction temperature and feed ratio. As shown in Table 2, with a fixed [HEA]/[CL]/[*t*-BuP$_2$] molar ratio of 20/80/1 and an increase in the polymerization temperature from 25 °C (HC-1 in Table 2) to 60 °C (HC-2 in Table 2), M_w increased from 1.26 × 10^4 g·mol^{-1} to 3.13 × 10^4 g·mol^{-1}. However, $Đ$ increased from 1.42 to 4.39. Furthermore, gelation occurred when the reaction time was prolonged to 32 h (HC-3). These results suggest that a low temperature was most suitable for this polymerization. Besides, changing the [HEA]/[CL] molar ratio from 10/90 to 90/10, M_w decreased dramatically from 1.38 × 10^4 g·mol^{-1} (HC-4) to 0.22 × 10^4 g·mol^{-1} (HC-6), but $Đ$ increased from 1.45 to 2.95. The possible reason is the decreasing amount of CL reduced the incidence of ROP, which is the key factor for the high molecular weight of the resulting polymer. The DSC curve suggests completely amorphous structures for HC-5 and HC-6 (Fig. S6 in ESI). Anyhow, high monomer conversions of both HEA and CL were obtained in all cases, and the molar fraction of HEA (F_{HEA}) in the copolymer determined by ^{1}H-NMR spectroscopy was approximately equal to the feed ratio, suggesting the possibility to adjust the polymeric structure by simply changing the monomer feed ratio.

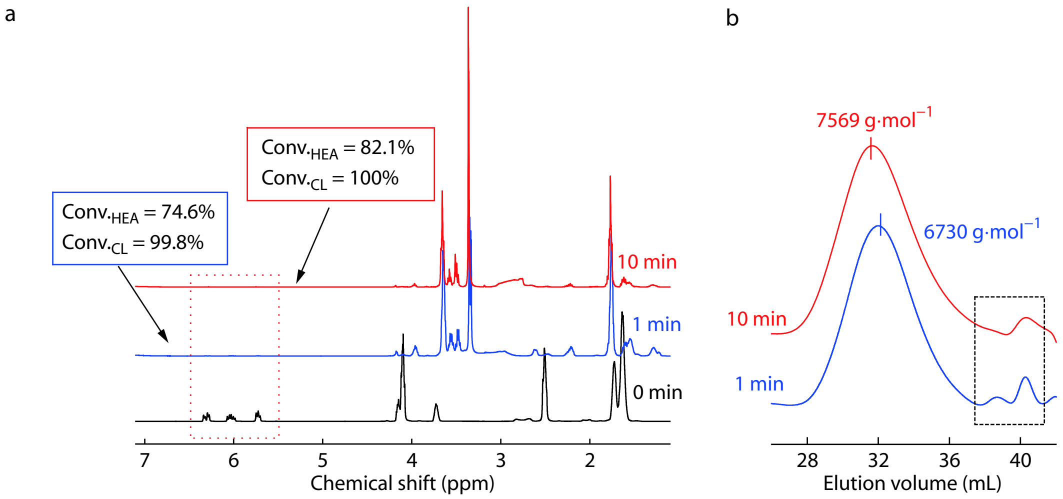


Fig. 8 (a) ^{1}H-NMR spectra and (b) dRI-GPC traces of samples taken at scheduled time intervals during the preparation of copolymer HC-1 at 25 °C.

CONCLUSIONS

In summary, we found that phosphazene bases could efficiently catalyze the proton transfer polymerization of 2-hydroxyethyl acrylate at room temperature, giving excellent monomer conversion. More importantly, phosphazene bases could also efficiently catalyze the hybrid copolymerization of 2-hydroxyethyl acrylate and ε-caprolactone. During this copolymerization, both monomers participated in the polymerization with high monomer conversions. Furthermore, the hybrid copolymerization was not realized according to the reported mechanism of ring-opening polymerization together with vinyl addition polymerization but rather by ring-opening polymerization combined with proton transfer polymerization. Hence, the resulting copolymers contained ester and ether structures in the backbone chains, endowing them with good hydrophilicity and degradability. Due to the numerous remarkable features, such as the high efficiency, mild reaction conditions, and simple product isolation, this new hybrid copolymerization may have wide applications in the fields of materials and chemistry.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2341-x.

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