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Synthesis of polyvinylethylene glycols (PVEGs) *via* polyetherification of vinylethylene carbonate by synergistic catalysis†

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An efficient and controllable polyetherification of vinylethylene carbonate (VEC) using diols as initiators is developed. By using a synergistic catalysis with palladium and boron reagents under mild conditions, the polymerization process enables the regioselective production of a series of polyvinylethylene glycols (PVEGs) bearing pendent vinyl groups in high yields with accurate molecular weight control and narrow molecular weight distribution. The utility of PVEGs is demonstrated by the production of functional polyurethanes and post-polymerization modification *via* thiol–ene photo-click chemistry.

The application of design criteria and practical technologies for molecular level control in organic synthesis to prepare well-defined macromolecules plays an important role in the discovery of new polymer materials with distinctive properties and functions. In particular, the application of these technologies in the polymerization of functional monomers to access polymers with pendent functional groups is a valuable tool for the variation of the structure and function of the macromolecules by post-polymerization modifications.[1] Nevertheless, the synthesis of functional polymers with precisely defined molecular weight, composition, and architecture still remains a formidable challenge. These polymerizations require not only efficient and accurate control, but also higher functional group tolerance. In addition, the introduction of versatile and reactive functional groups into the side chains of polymers is essential for the post-polymerization modifications. Therefore, the development of direct polymerization reactions using readily accessible monomers to prepare polymers with valuable pendent functional groups is still highly appealing.

Polyether polyols, mainly synthesized through ring-opening polymerization (ROP) of epoxides,[2] are widely used in the production of polyurethanes (PUs), surfactants and lubricants, as well as in the biomedical and cosmetic domains.[3] Although most of the functional groups are incompatible with the harsh ROP conditions, successful examples of synthesizing functional polyethers have been achieved using glycidyl ether derivatives as functional monomers.[2,4] Notably, allyl glycidyl ether (AGE) and ethoxyl vinyl glycidyl ether (EVGE) stand out as representative functional monomers, which allow the versatile vinyl group to be introduced into the chain of the polymers.[5] The pendent vinyl group can react with various thiols *via* thiol–ene click chemistry[6] to decorate polyethers with diverse pendant functionalities, thereby enabling the modification of both structure and function (Fig. 1A).[7]

Palladium-catalyzed allylic substitution is one of the most potent methods for carbon–carbon and carbon–heteroatom

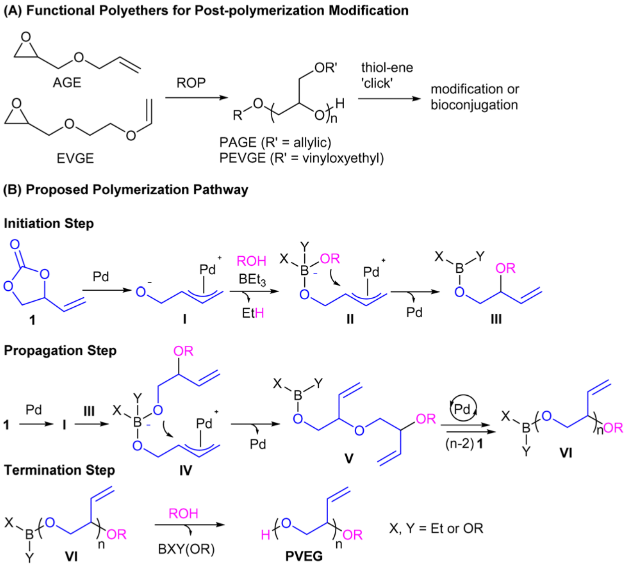

Fig. 1 (A) ROP of AGE and EVGE; (b) our strategy for the polymerization by synergistic catalysis.

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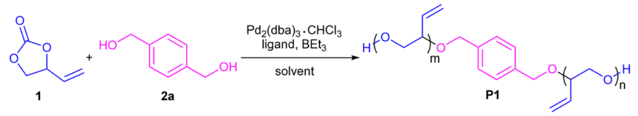
bond formation.[8] This useful organic transformation has been successfully applied to the polymerization by Nomura and colleagues.[9] However, this polymerization approach has generally been limited to polycondensation between bis-allylic monomers and malonate-type carbon nucleophiles to provide polymers bearing a carbon–carbon double bond on the main chain. Most recently, we developed regio- and stereoselective allylic etherification of substituted vinylethylene carbonates (VECs)[10] with water and alcohols under the cooperative catalysis system.[11] The catalytic reaction furnished functional ethylene glycols in almost quantitative yields with complete branched-regioselectivities. This efficient catalytic organic transformation inspired us to develop a novel polymerization approach for the synthesis of functional polyethylene glycols bearing a vinyl group on the side chain. We realized that commercially available VEC is an appropriate functional monomer. Our hypothesis is that VEC reacts with a palladium catalyst to afford the zwitterionic allylpalladium intermediate **I**, which can convert into boronate intermediate **II** by reaction with the boron reagent and capture alcohol as an initiator (Fig. 1B). This species would subsequently undergo nucleophilic addition with branched selectivity to afford reactive intermediate **III** to finish the initiation step.[11] Intermediate **III** would react with intermediate **I** generated from the reaction of VEC with a palladium catalyst to afford intermediate **IV** which undergoes regioselective etherification to give intermediate **V**. In the same manner under the cooperative catalysis system, leading to chain growth, the termination step would be achieved by releasing the borate with alcohol, resulting in the desired polyvinylethylene gylcols (PVEG). The boron cocatalyst will play an important role for the enhancement of the nucleophilicity of the alcohols and control the branched-selectivity of the etherification step.[11a] Herein, we report the successful implementation of this allylic etherification polymerization strategy and present a first efficient and controllable polyetherification approach that allows rapid access to vinyl-functional polyether diols with accurate molecular weight control and narrow molecular weight distribution. In addition, the utility of the obtained PVEGs is demonstrated by the synthesis of functional PU and the post-polymerization modification *via* thiol–ene photo-click chemistry.

Table 1 Optimization of the polymerization conditions[a]



Entry	Ligand	Solvent	Temp. (°C)/time (h)	Yield[b] (%)
1	dppp	THF	20/12	5
2	dppb	THF	20/12	20
3	BINAP	THF	20/12	80
4	DPEphos	THF	20/2	86
5	DPEphos	1,4-Dioxane	20/2	61
6	DPEphos	MTBE	20/2	75
7	DPEphos	Toluene	20/2	78
8	DPEphos	CH_2Cl_2	20/2	73
9	DPEphos	CH_3CN	20/2	76
10	DPEphos	THF	10/2	95
11	DPEphos	THF	50/2	91
13	DPEphos	THF	70/2	92
14[c]	DPEphos	THF	10/2	95

[a] Reaction conditions: **1** (1.0 mmol, 10 equiv.), **2a** (0.1 mmol, 1 equiv.), $Pd_2(dba)_3·CHCl_3$ (0.2 mol% for **1**), ligand (0.4 mol% for **1**), BEt_3 (0.4 mol% for **1**), solvent (1.0 mL). [b] Isolated yields. [c] The reaction carried out using $Pd_2(dba)_3·CHCl_3$ (0.15 mol% for **1**), DPEphos (0.3 mol% for **1**) and BEt_3 (0.3 mol% for **1**) under otherwise identical conditions.

Our initial studies focused on the optimization of allylic etherification polymerization of VEC **1** and 1,4-phenylenedimethanol (**2a**) as an initiator (Table 1). The identification of appropriate ligands for the polymerization of **1** (1.0 mmol, 10 equiv.) with **2a** (0.1 mmol, 1 equiv.) was firstly examined using a catalytic amount of $Pd_2(dba)_3·CHCl_3$ (0.2 mol% for **1**) as a palladium precursor and BEt_3 (0.4 mol% for **1**) in THF as a solvent at 20 °C (entries 1–4). As a result, we inspiringly found that the polymerization can finish within 2 h by using bis(2-diphenylphosphinophenyl)ether (DPEphos) as a ligand to produce the desired polyether diol **P1** in 86% isolated yield (entry 4). The solvent effect was next surveyed by using DPEphos as a ligand (entries 5–9), but no further improvement in the reaction efficiency was observed. It was found that the polymerization reaction is not sensitive to the reaction temperature (entries 10–13). These results indicated that the polyetherification is very reactive and almost no β-hydride elimination occurs.[10c] The best results were found at 10 °C to afford the product **P1** in up to 95% yield (entry 10). The polymerization proceeded smoothly when the palladium precursor was reduced to 0.15 mol% (entry 14). Finally, the optimal conditions were determined for synergistic catalysis including a palladium complex generated *in situ* from $Pd_2(dba)_3·CHCl_3$ (0.15 mol% for **1**) and DPEphos (0.3 mol% for **1**) and BEt_3 (0.3 mol% for **1**) in THF at 10 °C for 2 h (entry 14).

With the optimized conditions in hand, the catalytic polyetherification of VEC **1** with 10 times scale up by using various diol initiators was investigated (Fig. 2). The obtained polyether diol PVEGs (**P2–P12**) were characterized by nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) spectroscopies, and their hydroxyl values and molecular weight distributions were also assayed. Firstly, the different ratio of VEC **1** to initiator **2a** (1.0 mmol scale) for the polymerization under the optimized conditions was studied. To our delight, all polymerization reactions proceeded smoothly, yielding the desired PVEGs in almost quantitative yields. In addition, the molecular weight could be accurately controlled by the variation of the ratio of **1** to **2a**, and the produced polyether diols **P2–P6** showed narrow molecular weight distributions (PDI, 1.18–1.31). The molecular weight increased significantly with the increase of the ratio of **1** to **2b**, whereas the hydroxyl value decreased, albeit the chain growth was slowed down when the polymerization of **1** and **2a** was conducted at a ratio of 160 to 1 as determined by GPA analysis, as shown in Fig. 3A. The controlled polymerization could also be proved clearly by integration of the ratio of benzylic and vinylic protons in ^1H NMR spectrograms (Fig. 3B). The ratio of benzylic and vinyl protons increased remarkably from **P2** to **P6**. In addition, the

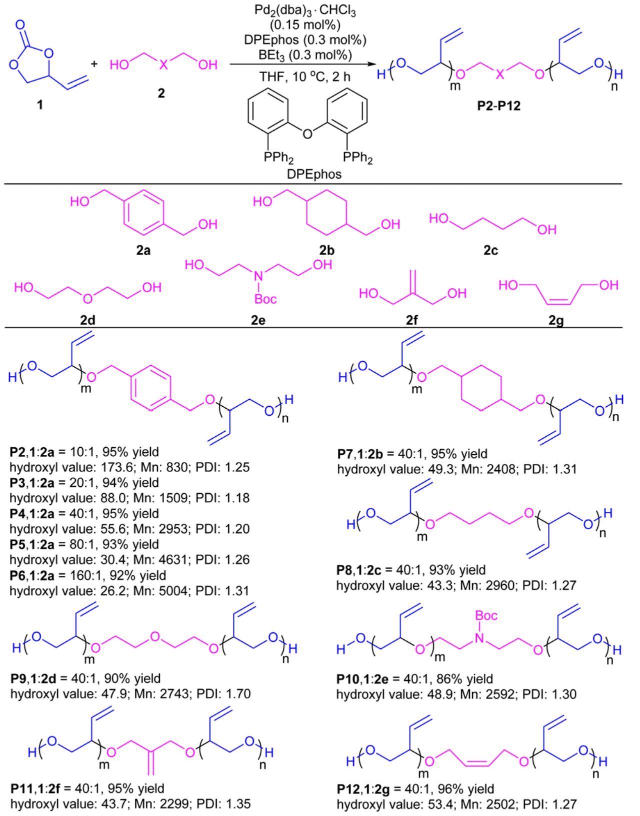
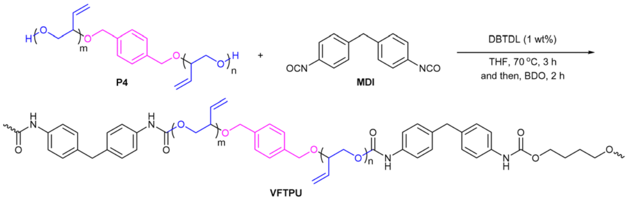


Fig. 2 Polyetherification of VEC with various diols as initiators by Pd/B synergistic catalysis. Reaction conditions: **2** (1.0 mmol, 1 equiv.), $Pd_2(dba)_3$·$CHCl_3$ (0.15 mol% for **1**), DPEphos (0.3 mol% for **1**), BEt_3 (0.3 mol% for **1**), THF (10.0 mL). The yields are of isolated materials. Hydroxyl value was measured according to the ASTM D4274 standard. M_n and polydispersity index (PDI) are determined by gel permeation chromatography (GPC) in THF, PDI = M_w/M_n.



Scheme 1 Synthesis of vinyl-functional TPU (VFTPU).

repeat unit was assayed as 70 g mol^{-1} by the determination of **P4** using MALDI-TOF MS spectroscopy (Fig. 3C), which further proved the correctness of the structure of the obtained PVEGs.

Next, the catalytic polyetherifications of VEC **1** with other diol initiators **2** (1 : 2 = 40) were investigated. As shown in Fig. 2, various diols could be accommodated under the polymerization conditions, yielding the corresponding PVEGs, namely **P7–P12**, in high yields with accurate molecular weight control and narrow molecular weight distributions. Notably, the ROP of propylene oxide produced polyether polyols with predominantly secondary hydroxyls,[12] which often lack sufficient reactivity with isocyanates for the production of PUs. As a distinct contrast, our catalytic polyetherification provided polyether diols with complete primary hydroxyl content.

In order to demonstrate the utility of the obtained PVEGs, the polyaddition of PVEG **P4** and 4,4′-diphenylmethane diisocyanate (MDI) was conducted using dibutyltin dilaurate (DBTDL) as a catalyst and 1,4-butadiol (BDO) as a chain extender in THF (Scheme 1). The polymerization proceeded smoothly to afford vinyl-functional thermoplastic polyurethane (VFTPU) in high yield with 20.9 kDa number average molecular weights (M_n). (For the details regarding the characterization of the obtained VFTPU, see the ESI†). Thermal properties of the VFTPU determined by thermal gravimetric analysis (TGA) showed that the thermal degradation behavior is consistent with the thermal properties for usual TPUs.[13] The thermomechanical properties of the VFTPU were next assessed by dynamic mechanical analysis (DMA). The results showed that the storage modulus (G') gradually increased at temperatures above 100 °C, indicating that the pendent vinyl group of VFTPU might undergo some degree of crosslinking at high temperature (Fig. S35c and Table S1, ESI†). Finally, the mechanical properties of the obtained VFTPU were also characterized by tensile tests (Fig. S35d, ESI†). The VFTPU exhibited the typical elastomer behavior, with a tensile strength of ∼780 Pa and a strain at break of ∼2490%.

The post-polymerization modification of PVEG **P4** was subsequently conducted *via* thiol–ene photo-click chemistry.[6] The

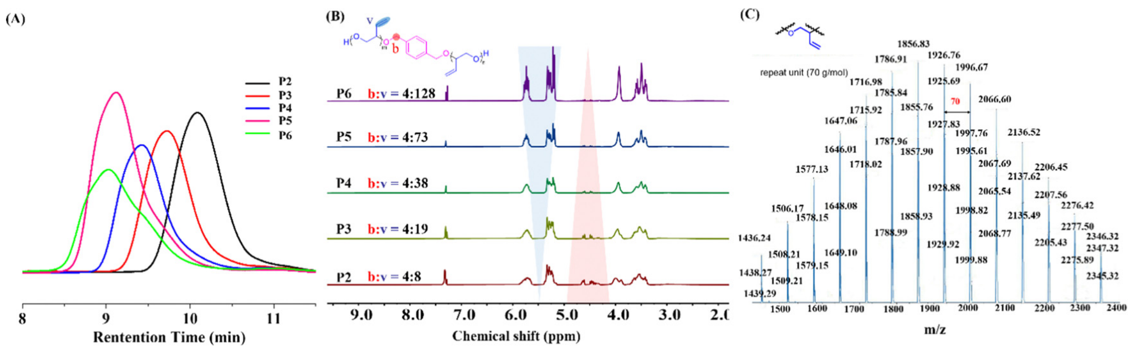


Fig. 3 Characterization of PVEGs. (A) Stack plot of GPC showing different ratios of **1** and **2a**. (B) Stack of the partial ^1H NMR spectrum (400 MHz, $CDCl_3$) highlighting the same peaks of benzylic (red) and vinylic (blue) protons for different ratios of **1** and **2a**. (C) MALDI-TOF MS spectrum of PVEG **P4** indicating that the repeat unit is 70 g mol^{-1}.

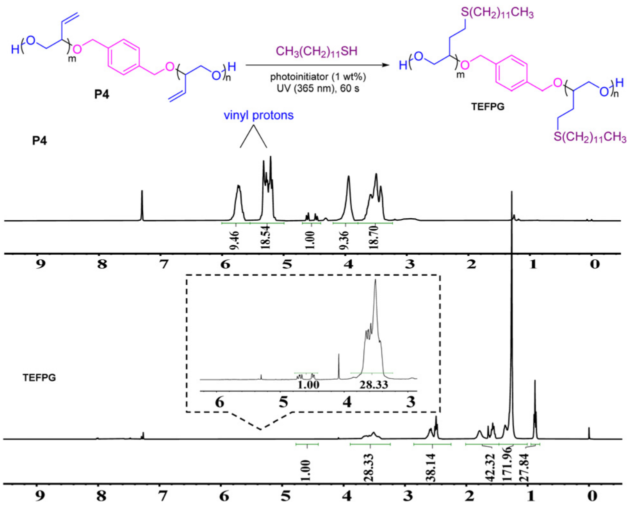


Fig. 4 Post-modification PVEG **P4** *via* thiol–ene chemistry and characterization by ^{1}H NMR.

post-modification was straightforwardly carried out by the UV (365 nm) irradiation of **P4** with excess 1-dodecanethiol in the presence of 2-hydroxy-2-methylpropiophenone (1 wt%) as a photoinitiator for 60 seconds, thus providing thioether-functional polyglycol (TEFPG) with very high efficiency. As shown in Fig. 4, the ^{1}H NMR spectrograms clearly indicated that the vinyl protons of **P4** disappeared completely after post-modification by the photo-click reaction. Correspondingly, the proton signals of $-CH_2SCH_2-$ and alkyl chains appeared in the ^{1}H NMR spectrogram of the produced TEFPG. These observations provide incontrovertible evidence of successful post-polymerization modification of pendent vinyl groups of PVEGs through efficient photo-click chemistry.

In conclusion, we have developed for the first time an efficient and controllable polyetherification of VEC **1** with diols **2** as initiators by a synergistic catalysis. By using a palladium complex and triethyl borane as a cooperative catalyst under mild neutral conditions, this polyetherification process effectively produced vinyl-functional PVEGs in high yields with complete branched-regioselectivities, accurate molecular weight control and narrow molecular weight distribution. The utility of the vinyl-functional PVEGs was demonstrated by the production of functional TPU and post-polymerization modification of the pendant vinyl group of PVEG using thiol–ene photo-click chemistry.

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Conflicts of interest

There are no conflicts of interest to declare.

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