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LIVING CATIONIC POLYMERIZATION OF β -(VINILOXY)ETHYL CINNAMATE

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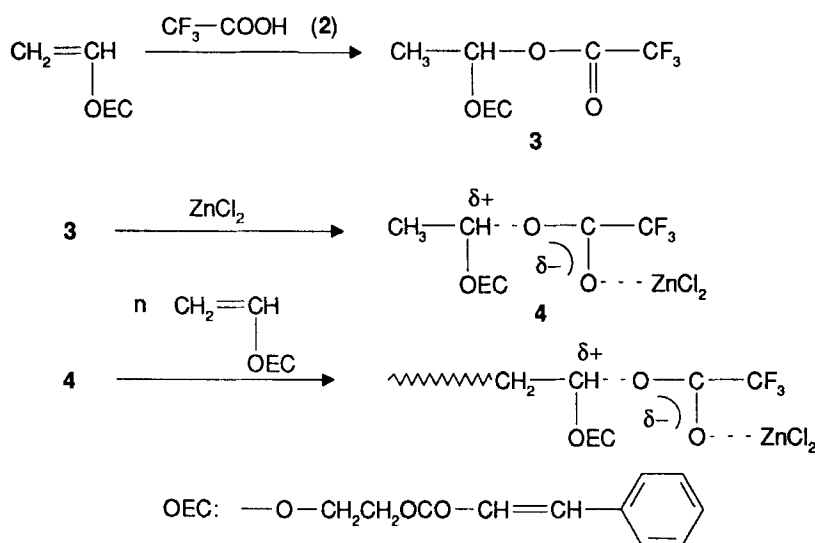
ABSTRACT

Trifluoroacetic acid and ZnCl_2 have been used as the initiating system for the living cationic polymerization of β -(viniloxy)ethyl cinnamate (VEC). In contrast to a previous initiating system [EtAlCl_2 and 1-(isobutoxy)ethyl acetate], the use of the new system led to excellent agreement between the molar masses of PVEC prepared and those calculated from monomer and trifluoroacetic acid feed ratios. The effect of temperature on the rate of VEC polymerization using this initiating system has been studied. Also reported is a comparison between the polymerization of VEC initiated using different Lewis acids and trifluoroacetic acid.

INTRODUCTION

In a previous paper [1] we reported the properties of polymer brushes formed from a poly[2-(viniloxy)ethyl cinnamate]-*block*-poly(isobutyl vinyl ether) (PVEC-*b*-PIBVE) diblock copolymer. The polymer brush formed could be photochemically cured by crosslinking the PVEC block. Crosslinked polymer brushes, as expected, possessed solvent and acid resistance. Important industrial applications were expected of crosslinked polymer brushes [2].

Poly[2-(viniloxy)ethyl cinnamate], active in photocrosslinking, is ideal for incorporation into a diblock copolymer for the preparation of crosslinked polymer brushes. We have reported the successful synthesis of PVEC-*b*-PIBVE and the



SCHEME 1.

cationic living polymerization of VEC in a previous paper [3] using EtAlCl_2 and 1-(isobutoxy)ethyl acetate (**1**) as the initiating system. The synthesis at that time was not optimal. The molar masses of PVEC or PVEC-*b*-PIBVE diblocks synthesized were always lower than those calculated from the monomer to **1** feed ratios. The lower molar masses were attributed to the polymerization of VEC by a transient product or products formed from reactions between protogenic impurities in VEC with EtAlCl_2 , which was in much excess compared to **1**.

We have since attempted the polymerization of VEC using another initiating system, i.e., trifluoroacetic acid (**2**)/ ZnCl_2 . Analogous to IBVE polymerization initiated by this system [4], the polymerization of VEC should proceed according to Scheme 1.

Using **2** and ZnCl_2 , excellent agreement between the molar masses of PVEC prepared and those calculated from $[\text{VEC}]/[\text{2}]$ feed ratios was obtained. In this paper we report the effect of temperature on the rate of VEC polymerization using this initiating system. We also report a comparison between the polymerization of VEC initiated using different Lewis acids and **2**.

EXPERIMENTAL

Materials

Toluene, 1,4-dioxane, and IBVE were purified by procedures described previously [3] and distilled over CaH_2 . Trifluoroacetic acid was stirred with phosphorus pentoxide overnight before distillation under argon. It was stored as a toluene solution in a refrigerator. EtAlCl_2 (Aldrich) was used without further purification. ZnCl_2 and ZnI_2 (Aldrich) were dried under reduced pressure and stored as ether solutions.

Monomer VEC was synthesized as described previously [3]. The monomer as a colorless oil was obtained by one of the following procedures. On a smaller scale, predistilled VEC was recrystallized from a dry hexane-toluene mixture at low temperature. The recrystallized VEC was vacuum distilled before polymerization. On a larger scale, predistilled VEC was stirred with freshly-cleft sodium at room temperature for 2 hours. This turned the liquid red. The excess sodium was filtered off and the VEC was distilled under reduced pressure.

Polymerization

The detailed procedure has been reported previously [3]. **3** was generated in-situ by the addition of **2** to a VEC solution in toluene at 0°C for 10 minutes [4]. For kinetic studies, the concentration of VEC was maintained at 1.09 g VEC in 10-mL toluene. The percentage conversion of VEC was followed by capillary gas chromatography using *n*-dodecane (~0.10 mL) as the internal standard. Samples taken by syringes were quenched with chilled methanol, washed with an aqueous saturated sodium bicarbonate solution and water, and dried over MgSO₄ before analysis.

Polymer Characterization

Molar masses of PVEC were determined by GPC using Styragel HR 4 (Waters) and Zorbax PSM 60-S (Chromatography Specialties) columns in series. The instrument was calibrated using polystyrene standards (Polysciences). The ¹H-NMR spectrum of a PVEC sample (CD₃Cl) is presented in Fig. 1.

RESULTS AND DISCUSSION

Temperature Effect

Monomer VEC was polymerized at -15, 0, and 21°C, and the kinetic results are presented in Fig. 2. As the temperature increased, the rate of polymerization

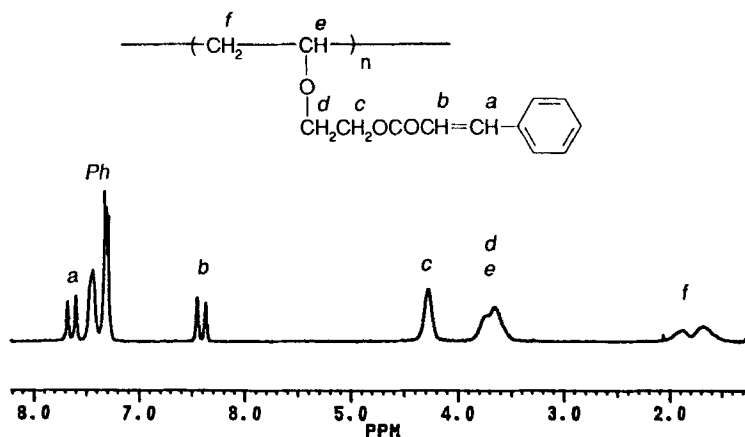


FIG. 1. The ¹H-NMR spectrum of a PVEC sample.

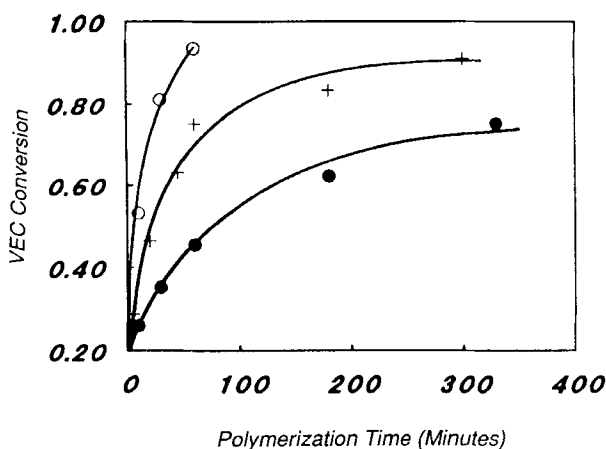


FIG. 2. Effect of temperature on the rate of VEC polymerization. The rate of polymerization is the highest at 21°C (○), lower at 0°C (+), and the lowest at -15°C (●). All polymerization mixtures had the following composition: 10 mL toluene, 1.09 g VEC, 1.0×10^{-4} mole **2** (0.50 M **2** in toluene, 0.20 mL), 1.0×10^{-4} mole ZnCl_2 (0.50 M ZnCl_2 in ether, 0.20 mL), and 0.112 g *n*-dodecane.

increased, as expected. At room temperature, the polymerization should be complete in ~ 2 hours.

At all temperatures examined, the polydispersity indices ($\overline{M}_w/\overline{M}_n$) remained low, i.e., ~ 1.16 if VEC conversion was higher than 50%. At conversions much lower than 50%, GPC chromatograms were not well resolved for the accurate evaluation of $\overline{M}_w/\overline{M}_n$.

In Fig. 3 the number-average molar masses \overline{M}_n of PVEC are plotted as a function VEC percentage conversion of polymerizations at 0 and -15°C. As VEC conversion increased, the PVEC molar mass increased. The \overline{M}_n -versus-conversion line obtained from experimental data is close to the calculated line. The small discrepancy might be due to the use of polystyrene as the GPC calibration standard. These results suggest the living nature of the polymerization.

Effect of Lewis Acids

Three other Lewis acids, ZnI_2 , EtAlCl_2 , and $\text{Ti}(\text{OPr}^i)_4$, where OPr^i stands for isopropoxy, were used to replace ZnCl_2 in the initiating system. $\text{Ti}(\text{OPr}^i)_4$ and **2** did not lead to polymerization. The kinetic results of VEC polymerization using the other Lewis acids are compared in Fig. 4. In all cases, an equal molar equivalent of Lewis acid and **2** was used.

That the replacement of ZnCl_2 with a weak Lewis acid $\text{Ti}(\text{OPr}^i)_4$ did not lead to polymerization is understandable by examining Scheme 1. For VEC polymerization to occur, the Lewis acid should be strong so that a partially charge-separated species similar to **4** can form. As the strength of the Lewis acid decreases, the extent of VEC cationic feature in a transient species similar to **4** decreases, and thus the rate of polymerization decreases. $\text{Ti}(\text{OPr}^i)_4$ did not initiate polymerization because

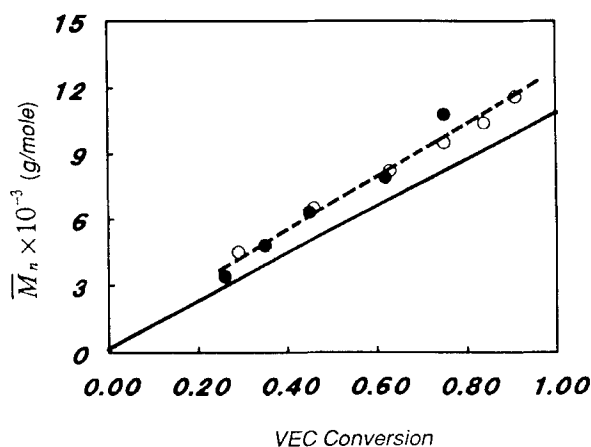


FIG. 3. Increase in the number-average molar mass as a function of VEC percentage conversion. The solid-line curve and the dashed-line curve represent the theoretical and experimental lines, respectively. The experimental line is constructed by fitting data obtained at polymerization temperatures 0°C (○) and -15°C (●), respectively.

it is too weak a Lewis acid. ZnI_2 is a stronger Lewis acid than $\text{Ti}(\text{OPr}^i)_4$ but weaker than ZnCl_2 , and the rate of VEC polymerization by ZnI_2 plus **2** was slower, as expected, than that of ZnCl_2 plus **2** (see Fig. 4).

The strongest Lewis acid examined was EtAlCl_2 . VEC polymerization would have been fast and nonliving with the use of EtAlCl_2 plus **2** as the initiating system [4]. To stabilize the partially charge-separated species formed, dioxane was added in the polymerization mixture [4]. Added dioxane, however, slowed down the rate of VEC polymerization.

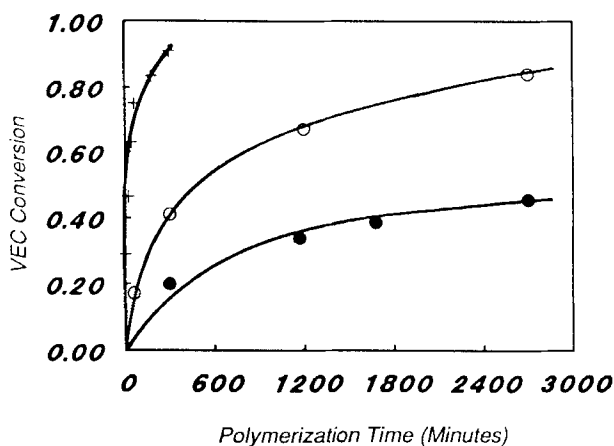


FIG. 4. Effect of Lewis acids. The use of **2** and 1 molar equivalent of ZnCl_2 led to the highest polymerization rate (+). The rate decreased as ZnCl_2 was replaced by ZnI_2 (○) and EtAlCl_2 (●).

TABLE 1. Comparison between PVEC Molar Masses Obtained Experimentally and Those Calculated from [VEC]/[2] Feed Ratios Using 2 and ZnCl₂ as the Initiating System

Calcd. \bar{M}_n (g/mol)	GPC \bar{M}_n (g/mol)	GPC \bar{M}_w (g/mol)	\bar{M}_w/\bar{M}_n
1.09×10^4	1.16×10^4	1.39×10^4	1.20
2.18×10^4	2.06×10^4	2.40×10^4	1.17

The polydispersity of PVEC produced decreased as the rate of polymerization decreased. At sufficiently high VEC conversions (> 50%), PVEC had the highest polydispersity, i.e., ~1.19, when produced using 2 and ZnCl₂ as the initiating system. Polydispersity decreased to ~1.09 when 2 and ZnI₂ were used. The lowest polydispersity, i.e., ~1.06, was observed when 2 and EtAlCl₂ was used as the initiating system. This can be explained as follows. If the rate of initiation is assumed not to vary significantly with the strength of the Lewis acids, a decrease in the rate of propagation will ensure that all chains will grow simultaneously, leading to a more monodispersed product.

Comparison with VEC Polymerization Initiated by 1 Plus EtAlCl₂

The polymerization of VEC by 1 plus EtAlCl₂ led to polymers with molar masses considerably lower than those expected [3]. This has been attributed to initiation of VEC polymerization by a product/products formed from the reaction between the excess EtAlCl₂ with protogenic impurities in VEC.

The use of 2 plus ZnCl₂ as the initiating system led to PVEC with molar masses very close to those calculated from [VEC]/[2] feed ratios as shown in Table 1 for two samples. The excellent agreement is probably because equal molar equivalents of 2 and ZnCl₂ were used and no excess ZnCl₂ was left to react with protogenic impurities to initiate additional VEC polymerization.

The absence of side initiation has been further verified by the successful block copolymerization of VEC using PIBVE cations, prepared by initiating IBVE polymerization with 2 plus ZnCl₂, to produce PIBVE-*b*-PVEC with polydispersities typically lower than 1.18. The block copolymerization of VEC using PIBVE cations prepared by initiating IBVE polymerization with 1 and EtAlCl₂ was previously shown to lead to polymers with bimodal molar mass distributions [3].

As expected, PVEC cations also initiated IBVE polymerization to produce PVEC-*b*-PIBVE with calculated molar masses.

CONCLUSION

Combinations of trifluoroacetic acid and ZnCl₂ have been shown to initiate the polymerization of VEC to produce PVEC with close to calculated molar masses. The rate of VEC polymerization using this initiating system increased with temperature, and the polymerization stayed living over the -15 to 21 °C temperature range.

When different Lewis acids were used to replace $ZnCl_2$, the rate of VEC polymerization decreased with the decreasing strength of the Lewis acid, as did the polydispersity index of the PVEC produced.

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