A novel synthetic route to highly cross-linked poly(alkylvinylether)s

Synthesis and free radical polymerization of ethyl vinyl ethers containing the electron acceptors benzylidenemalononitrile and benzylidenecyanoacetate

Ju-Yeon Lee

Department of Chemistry, Inje University, Aebang-dong, Kimhae 621-749, Seoul, Korea
(Fax 05 25-21-9718)

Received: 16 November 1995/Revised version: 22 January 1996/Accepted: 30 January 1996

Summary

p-(2-Vinylxyethoxy)benzylidenemalononitrile (3) and methyl p-(2-vinylxyethoxy)benzylidenecyanoacetate (4) was prepared by the condensation of p-(2-vinylxyethoxy)benzaldehyde with malononitile or methyl cyanoacetate, respectively. Vinyl ether monomers 3 and 4 polymerized quantitatively with radical initiators in γ-butyrolactone solution at 65°C. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerization of 3 and 4 led to swelling polymers 5 and 6 that were not soluble in common solvents due to cross-linking. Under the same polymerization conditions ethyl vinyl ether polymerized well with model compounds of p-methoxybenzylidenemalononitrile and methyl p-methoxybenzylidenecyanoacetate, respectively, to give 1:1 alternating copolymers 9 and 10 in high yields. Alternating copolymers 9 and 10 were soluble in common solvents such as acetone and DMSO, and the inherent viscosities of the polymers were in the range of 0.36-0.74 dL/g. Films cast from acetone solution were cloudy and tough and T_g values obtained from DSC thermograms were in the range of 59-60°C.

Introduction

It is well known that electron-rich alkyl vinyl ethers do not radically homopolymerize, but copolymerize well with vinyl monomers of electron deficient character such as vinylidene cyanide (1), 2-vinylcyclopropane-1,1-dicyanomethylene (2), alkyl α-cyanoacrylates (3-5), alkyl vinyl ketones (6), maleic anhydride, and others by radical initiation. Cycloadditions frequently accompanied these polymerizations and most of the cyclic adducts are cyclobutane compounds. For example, alkyl vinyl ethers readily form cyclobutane adducts with a variety of electron-poor olefins such as tetracyanoethylene (7) and tricyanoethylene (8). 3,4-Dihydro-2H-pyrans are formed in the reactions of alkyl vinyl ethers with alkyl α-cyanoacrylates, dimethyl dicyanofumarate (9), and alkyl vinyl ketones (6). These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species (10). It has been reported that trisubstituted electron-poor olefins such as benzylidenemalononitrile and ethyl benzylidenecyanoacetate do not homopolymerize, but copolymerize with vinyl acetate, styrene, acrylonitrile, or methyl acrylate by radical initiators(11-17). The question remains as to
whether certain bifunctional monomers composed of electron–rich alkyl vinyl ether and electron–poor trisubstituted olefin can be polymerized by radical initiation. Thus, it is of interest to prepare alkyl vinyl ethers containing electron acceptors in the side chain and polymerize by using radical initiators. In this work we prepared two ethyl vinyl ethers containing the electron acceptors benzylidene malononitrile and benzylidene cyanoacetate in the side chain, and investigated their polymerization behaviors. The present report describes the synthesis and radical polymerization of p-(2-vinyl oxyethoxy) benzylidene malononitrile (3) and methyl p-(2-vinyl oxyethoxy) benzylidene cyanoacetate (4). We now report the results of the initial phase of the work.

**Experimental**

**Materials**
The reagent grade chemicals were purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether was distilled. Sodium iodide was dried for 4 h at 100°C under vacuum. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation under reduced pressure. p-Hydroxybenzaldehyde was recrystallized from water and dried under vacuum. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. Methyl cyanoacetate and n-butanol were dried with anhydrous magnesium sulfate and distilled under nitrogen. γ-Butyrolactone was dried with anhydrous magnesium sulfate and distilled under nitrogen. Piperidine was dried with calcium hydride and fractionally distilled. AIBN was recrystallized from methanol and dried under reduced pressure at room temperature. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described (21).

**Measurements**
IR spectra were taken on a Hitachi Model 260–30 infrared spectrophotometer. Proton-NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyzer. The glass transition temperatures (Tg) were measured on a DuPont 910 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min up to 700°C was used for the thermal degradation study of polymers under nitrogen. Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon–Fenske viscometer.

**Preparation of p-(2-vinyl oxyethoxy) benzaldehyde (2)**
4-Hydroxybenzaldehyde (12.2 g, 0.10 mol), anhydrous potassium carbonate (18.0 g, 0.13 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 180 mL of dry acetone under nitrogen. The mixture was refluxed in an oil bath kept at 60°C for 72 h under nitrogen. The resulting solution was cooled to room temperature, and filtered, and the inorganic salts were washed with 50 mL of acetone. Rotary evaporation of acetone gave crude product, which on vacuum distillation yielded 16.3 g (85% yield) of pure product 2. Bp: 72–74°C (0.2 mmHg). Compound 2 was crystallized in the refrigerator (6°C). Proton-NMR (acetone-d6) δ 9.89 (1H, s), 7.63–7.99 (2H, m), 6.87–7.28 (2H, m), 6.32–6.73 (1H, q), 4.18–4.48 (2H, m), 3.70–4.17 (4H, m). IR (neat) 3119, 3068, 2940, 2878, 2833 (C–H), 1694, 1603, 1579 (C–C) cm⁻¹.

**Preparation of p-(2-vinyl oxyethoxy) benzylidene malononitrile (3)**
Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2 (5.38 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 50 mL of n-butanol with stirring at 0°C.