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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

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Summary

p-(2-Vinyloxyethoxy)benzylidenemalononitrile (3) and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate (4) was prepared by the condensation of p-(2-vinyloxyethoxy)benzaldehyde with malononitrile 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-dicarbonitrile (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 intrest 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 benzylidenemalononitrile and benzylidenecyanoacetate in the side chain. and investigated their polymerization behaviors. The present report describes the synthesis and radical polymerization of p-(2-vinyloxyethoxy)benzylidenemalononitrile (3) and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate (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 4h 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. α,α'-Azobisisobutyronitrile (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 (T_g) 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-vinyloxyethoxy)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-d_6) 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-vinyloxyethoxy)benzylidenemalononitrile (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 under nitrogen. After stirring for 1 h at 0°C, the product was filtered and washed successively with cold n-butanol (80 mL), water (30 mL), and cold n-butanol (20 mL). The obtained pale yellow product was recrystallized from n-butanol to give 5.38 g (80% yield) of **3**. Mp: 80-82°C. Proton-NMR (acetone-d_6) δ 7.75-8.13 (3H, m), 6.83-7.28 (2H, m), 6.30-6.73 (1H, q), 4.20-4.51 (2H, m), 3.76-4.21 (4H, m). IR (KBr) 3105, 3067, 2938, 2869 (C-H), 2230 (CN), 1628, 1603, 1579 (C=C) cm^{-1}. Anal. Calcd for $C_{14}H_{12}N_2O_2$:C, 69.99; H, 5.03; N, 11.66. Found: C, 69.90; H, 5.08; N, 11.58.

Preparation of methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate (4)

Piperidine (0.17 g, 2.0 mmol) was added to a solution of 2 (5.77 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 45 mL of n-butanol with stirring at 0°C under nitrogen. The resulting solution was stirred for 1 h at 0°C and 10 h at room temperature. After cooling in an ice bath, the product was filtered and washed successively with cold n-butanol (30 mL), water (50 mL), and cold n-butanol (20 mL). The obtained pale yellow product was recrystallized from n-butanol to give 5.90 g (72% yield) of 4. Mp: 95-97°C. Proton-NMR (acetone-d_6) δ 7.84-8.25 (3H, m), 6.93-7.29 (2H, m), 6.32-6.75 (1H, q), 4.25-4.50 (2H, m), 3.87-4.24 (4H, m), 3.88 (3H, s). IR (KBr) 3103, 3016, 2957, 2930 (C-H), 2220 (CN), 1726 (C=O), 1618, 1588 (C=C) cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO_4$:C, 65.92; H, 5.53; N, 5.13. Found: C, 65.85; H, 5.49; N, 5.18.

Preparation of p-methoxybenzylidenemalononitrile (7)

p-Methoxybenzylidenemalononitrile (7) was prepared according to the literature procedure (7) by condensing p-anisaldehyde with malononitrile in n-butanol in the presence of piperidine as catalyst. 7: 95% yield. Mp: 114-115°C [lit. (7) 114.5-115°C]. ^{1}H NMR (acetone-d_6) δ 7.86-8.17 (3H, m), 6.97-7.27 (2H, m), 3.93 (3H, s). IR (KBr) 2215 (CN), 1597, 1563, 1508 (C=C) cm^{-1}.

Preparation of Methyl p-methoxybenzylidenecyanoacetate (8)

Methyl p-methoxybenzylidenecyanoacetate (8) was prepared according to the literature procedure (7) by condensing p-anisaldehyde with methyl cyanoacetate in n-butanol in the presence of piperidine as catalyst. 8: 88% yield. Mp: 98-99°C. ^{1}H NMR (acetone-d_6) δ 7.92-8.26 (3H, m), 6.95-7.25 (2H, m), 3.91 (3H, s), 3.86 (3H, s). IR (KBr) 2205 (CN), 1714 (C=O), 1574, 1552, 1504 (C=C) cm^{-1}.

Radical polymerizations of p-(2-vinyloxyethoxy)benzylidenemalononitrile (3) *and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate* (4)

A representative radical polymerization procedure (the case of **3**) was as follows: In a polymerization tube were placed 0.48 g (2.0 mmol) of **3**, 1.97 mg (0.012 mmol) of AIBN, and 2.0 mL of γ-butyrolactone under nitrogen. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 65°C. After 2 h the polymerization tube was opened and the swelling polymer was poured into 400 mL of methanol. The precipitated polymer was collected and dried under vacum to give 0.48 g (100% yield) of polymer 5. IR (KBr) 3021 (=C-H), 2928, 2872 (C-H), 2220 (CN), 1604, 1577, 1555, 1508 (C=C) cm^{-1}. Anal. Calcd for$(C_{14}H_{12}N_2O_2)_n$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.90; H, 5.12; N, 11.57. 6: 100% yield. IR (KBr) 3025 (=C-H), 2950, 2873 (C-H), 2218 (CN), 1735 (C=O), 1605, 1591, 1511 (C=C) cm^{-1}. Anal. Calcd for $(C_{15}H_{15}NO_4)_n$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.83; H, 5.45; N, 5.21.

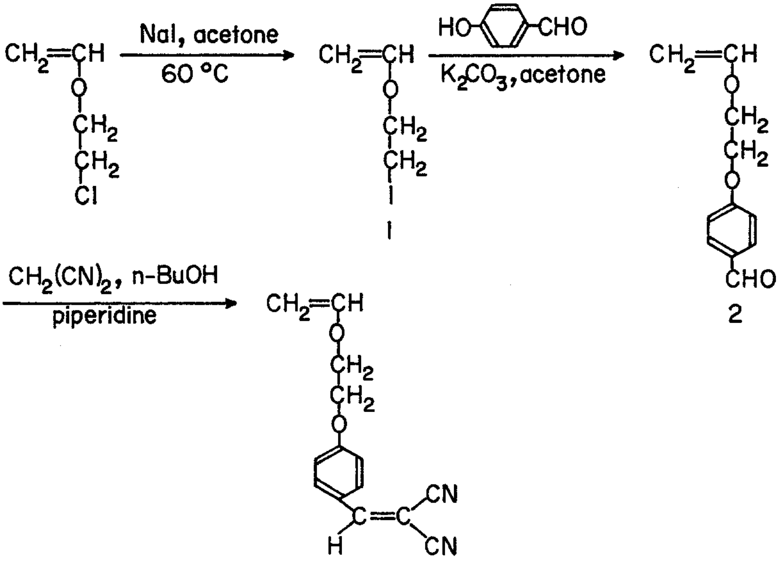
Radical copolymerizations of p-methoxybenzylidenemalononitrile (7) *and methyl p-methoxybenzylidenecyanoacetate* (8)

A representative radical polymerization procedure (the case of **7**) was as follows: In a polymerization tube were placed 0.27 g (1.5 mmol) of **7**, 0.11 g (1.5 mmol) of ethyl vinyl ether, 3.0 mg (0.018 mmol) of AIBN, and 1.8 mL of γ -butyrolactone under nitrogen. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 65°C. After 3 h the polymerization tube was opened and the viscous polymer solution was poured into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol. Thus obtained white polymer was dried under vacum to give 0.36 g (96% yield) of polymer 9; η_{inh} = 0.74 dL/g (c 0.5 g/dL in acetone at 25°C). ^{1}H NMR (acetone-d_6) δ 6.18-7.33 (4H, m), 3.40-4.63 (6H, m), 2.83-3.37 (1H, m), 1.50-2.27 (2H, m), 0.72-1.47 (3H, m). IR (KBr) 2972, 2930, 2895, 2833 (C-H), 2235 (CN), 1610, 1577, 1512 (C=C) cm^{-1}. Anal. Calcd for($C_{15}H_{16}N_2O_2$)$_n$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.20; H, 6.21; N, 11.02. 10: ^{1}H NMR (acetone-d_6) δ 6.11-7.50 (4H, m), 2.88-4.17 (9H, m), 2.12-2.85 (1H, m), 1.30-1.93 (2H, m), 0.51-1.27 (3H, m). IR (KBr) 2972, 2950, 2895, 2832 (C-H), 2233 (CN), 1738 (C=O), 1606, 1575, 1508 (C=C) cm^{-1}. Anal. Calcd for ($C_{16}H_{19}NO_4$)$_n$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.48; H, 6.55; N, 4.92.

Results and Discussion

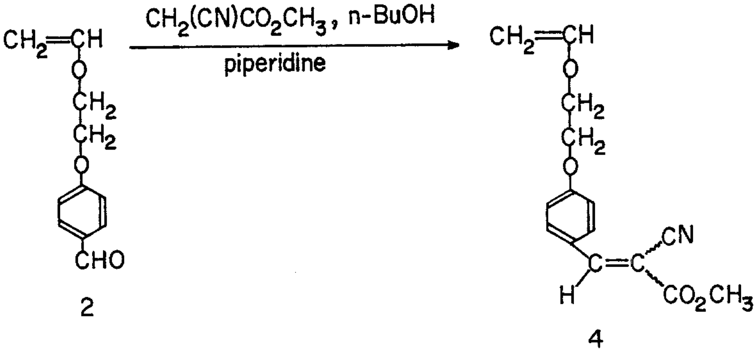
Syntheses of monomers 3 *and* 4

2-Iodoethyl vinyl ether (1) was prepared by the well known halogen exchange reaction (18) from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 4-hydroxybenaldehyde to yield p-(2-vinyloxyethoxy)benzaldehyde (2) (19). p-(2-Vinyloxyethoxy)benzylidenemalononitrile (3) and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate (4) were synthesized by the condensation of 2 with malononitrile or methyl cyanoacetate, respectively (20). The chemical structure of the compounds was confirmed by proton-NMR, and IR spectra, and elemental analysis. Spectral data indicated that compound 4 was a mixture of the cis- and trans-isomer.



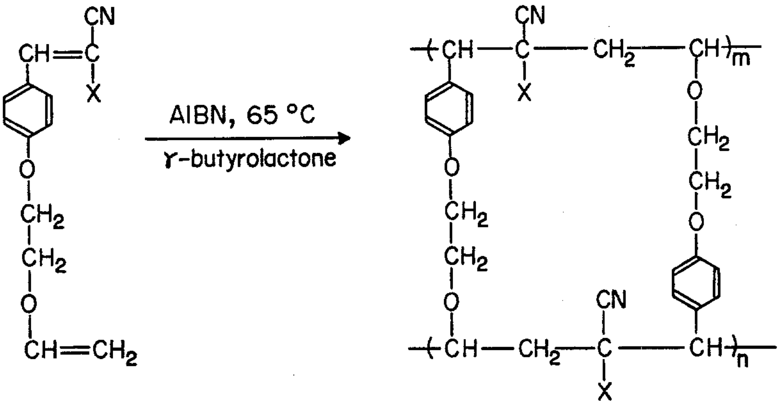
2

3



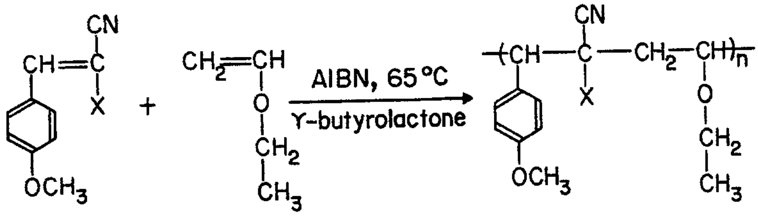
Radical polymerizations of monomers **3** *and* **4**

p-(2-Vinyloxyethoxy)benzylidenemalononitrile (3) and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate (4) were plymerized in γ-butyrolactone solution at 65°C with AIBN as radical initiator to give polymers **5** and **6**. The polymerization results are summarized in Table 1. Monomers **3** and **4** were quite reactive toward radical initiator and polymerized readily. The polymerizabilities of the monomers toward radical initiator were very high and in all cases, **3** and **4** polymerized quantitatively by AIBN at 65 °C within 3 h. The chemical structures of the polymers were identified by IR spectra and elemental analyses. The IR spectra confirmed the chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the polymers. Recently we have reported the vinyl poymerization of monomers **3** and **4** by cationic initiators without cross-linking (21). In contrast to that report, the trisubstituted terminal double bond participated in the vinyl polymerization, and radical polymerization of **3** and **4** led only to optically trasparent swelling polymers **5** and **6**. Polymers **5** and **6** were not soluble in any organic solvents due to cross-linking. Thus, we have found a unique polymerization system that lead to highly cross-linked poly(alkylvinylether)s by radical initiators.



2, X=CN
3, X=CO_2CH_3

4, X=CN
5, X=CO_2CH_3



6, X=CN
7, X=CO_2CH_3

8, X=CN
9, X=CO_2CH_3

Table 1. Free radical polymerizations of 3[a] and 4[b] by AIBN in γ-butyrolactone at 65°C

Monomer	Monomer/Solvent (mol/1 L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
3	1.00	0.6	2	100
3	0.67	0.8	3	100
3	0.33	1.0	4	100
3	0.25	3.0	4	100
4	1.00	0.6	2	100
4	0.67	0.8	3	100
4	0.33	1.0	4	100
4	0.25	3.0	5	100

[a] **3** = p-(2-Vinyloxyethoxy)benzylidenemalononitrile.
[b] **4** = Methyl p-(2-Vinyloxyethoxy)benzylidenecyanoacetate.

Table 2. Free radical copolymerizations[a] of **7** and **8** with ethyl vinyl ether by AIBN in γ-butyrolactone at 65°C

Monomer[b]	Monomer/Solvent (mol/1 L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)	η_{inh}[c] (dL/g)
7/EVE, 1/1	1.67	0.6	3	96	0.74
7/EVE, 1/2	1.20	0.8	3	98	0.68
7/EVE, 1/2	1.00	1.0	4	98	0.56
7/EVE, 1/3	1.00	3.0	4	97	0.48
8/EVE, 1/1	1.67	0.6	3	94	0.66
8/EVE, 1/2	1.20	0.8	3	98	0.60
8/EVE, 1/2	1.00	1.0	4	96	0.52
8/EVE, 1/3	1.00	3.0	5	96	0.36

[a] The copolymer compositions were estimated to be 1:1 by ^1H NMR spectra and elemental analyses. [b] **7** = p-Mthoxybenzylidenemalononitrile; EVE = ethyl vinyl ether; **8** = methyl p-methoxybenzylidenecyanoacetate; [c] Inherent viscosity of polymer: 0.5 g/dL in acetone at 25°C.

Furthermore, the striking feature of this particular polymerization system is that it provides an unprecedented radical polymerization of alkyl vinyl ethers which do not polymerize radically. To investigate if the cross-linking was due to the terminal double bond, ethyl vinyl ether was polymerized by AIBN at 65°C in the presence of p-methoxybenzylidenemalononitrile (7) and methyl p-methoxybenzylidenecyanoacetate (8), respectively. The resulting copolymers were isolated by reprecipitation from acetone solution into methanol. The copolymerization results are summarized in Table 2. From the data shown in Table 2 it was found that compounds **7** and **8** copolymerized well with ethyl vinyl ether by AIBN as free radical initiator to give high molecular weight (η_{inh}=0.74 dL.g) copolymers **9** and **10** in high yields. Elemental analyses and spectral data indicated that the polymer obtained in each case was 1:1 alternating copolymer of both monomers. These experimental results are resonable in view of the fact that **7** and **8** are strong electron-acceptor olefins and ethyl vinyl ether is a strong electron-donor momoner. The alternating copolymers **9** and **10** were white amorphous materials that were soluble in acetone and DMSO, but insoluble in methanol and diethyl ether. The inherent viscosities of polymers **9** and **10** were in the range of 0.36-0.74 dL/g. Polymers **9** and **10** have good film-forming properties and films cast from acetone solution were cloudy and quite tough. The thermal behaviors of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 3. Polymers **5** and **6** showed a good thermal stability and did not decompose below 300°C as shown in Table 3. The polymers show a double phase degradation pattern in their TGA thermograms, probably due to cross-linking. Cross-linked polymers **5** and **6** showed broad endothermic bands around 75-110°C without any characteristic T_g peaks in DSC thermograms. Alternating copolymers **9** and **10** showed a thermal stability up to 270°C and the T_g values of the polymers were around 59-60 °C. These T_g values are higher than those for poly(ethyl vinyl ether) (-43°C), probably due to the presence of polar pendant group.

Table 3. Thermal properties of polymers

Polymer	T_g^a, °C	Degradation temp, °C[b]			Residue[b] at 700°C, %
		5%-loss	20%-loss	40%-loss	
5	-	310	338	430	6.67
6	-	305	340	384	4.62
9	60	271	303	332	8.24
10	59	265	297	335	2.92

[a] Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere.
[b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

In conclusion, we prepared ethyl vinyl ethers **3** and **4** containing electron acceptors, benzylidenemalononitrile and benzylidenecyanoacetate. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerization of **3** and **4** led to highly cross-linked polymers quantitatively. Model compounds **7** and **8** readily copolymerized with ethyl vinyl ether under the polymerization conditions by radical initiators to give 1:1 alternating copolymers **9** and **10** in high yields, which support the high polymerizabilities of monomers **3** and **4** toward radical initiators. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported later.

Acknowledgements

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