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Synthesis of sterically hindered ethyl vinyl ethers containing electron acceptors and their polymerization behaviors

Ju-Yeon Lee *, Hyun-Ju Lee, Moo-Yong Kim

Department of Chemistry, Inje University, 607 Aebang-dong, Kimhae 621-749, Seoul, Korea

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Summary

3,5-Dimethoxy-4-(2'-vinyloxyethoxy)benzylidenemalononitrile (2) and methyl 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenecyanoacetate (3) were prepared and polymerized by radical and cationic initiators. Bifunctional monomers 2 and 3 did not polymerize by radical initiators, but copolymerized readily with ethyl vinyl ether in γ-butyrolactone solution at 65°C. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerization of 2 and 3 with ethyl vinyl ether led to swelling polymers 8 and 9 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 3,4,5-trimethoxybenzylidenemalononitrile (10) and methyl 3,4,5-trimethoxybenzylidenecyanoacetate (11), respectively, to give 1:1 alternating copolymers 12 and 13 in high yields. Polymers 8 and 9 showed a thermal stability up to 300°C without any characteristic T_g peaks in DSC thermograms. Alternating copolymers 12 and 13 were soluble in common solvents such as acetone and DMSO, and the inherent viscosities of the polymers were in the range of 0.33-0.55 dL/g. Films of polymers 12 and 13 cast from acetone solution were cloudy and tough and T_g values obtained from DSC thermograms were in the range of 163-168°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

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* Corresponding author

homopolymerize, but copolymerize with vinyl acetate, styrene, acrylonitrile, or methyl acrylate by radical initiators(11-15). 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. Recently we have prepared p-(2-vinyloxyethoxy)benzylidenemalononitrile and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate, and polymerized by radical initiators (16). These bifunctional ethyl vinyl ethers polymerized quantitatively with radical initiators to give swelling polymers that were not soluble in organic solvents due to cross-linking. This work is now extended with the syntheses and radical polymerizations of another ethy vinyl ethers containing electron acceptors. Vinyl ether moieties of these compounds are sterically very hindered and showed abnormal polymerization behaviors. In this work we prepared sterically crowed ethyl vinyl ethers containing the electron acceptors 3,4,5-trialkoxybenzylidenemalononitrile and 3,4,5-trialkoxybenzylidenecyanoacetate in the side chain and investigated their polymerization behaviors. The present report describes the syntheses and radical polymerizations of 3,5-dimethoxy-4-(2′-vinyloxyethoxy)benzylidenemalononitrile (2) and methyl 3,5-dimethoxy-4-(2′-vinyloxyethoxy)benzylidenecyanoacetate (3). We now report the results of the initial phase of the work.

Experimental

3,5-Dimethoxy-4-(2′-vinyloxyethoxy)benzaldehyde (1)

Compound 1 was prepared according to the literature (16) procedure from 2-iodoethyl vinyl ether and 3,5-dimethoxy-4-hydroxybenzaldehyde, and was recrystallized fromo n-butanol. Mp, 44-45 °C. ^{1}H NMR (acetone-d_6) δ 3.85 (s, 2 CH_3O-), 3.86-4.38 (m, CH_2= and -O-CH_2-CH_2-O-), 6.18-6.67 (q, =CH-O-), 7.13 (s, aromatic), 9.78 (s, -CH=O). IR (KBr) 3013 (m, =C-H), 2975, 2955, 2940, 2836 (s, C-H), 1691, 1677 (vs, C=O), 1627, 1578 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.84; H, 6.36.

3,5-Dimethoxy-4-(2′-vinyloxyethoxy)benzylidenemalononitrile (2)

Compound 2 was prepared according to the literature (16) procedure from 3,5-dimethoxy-4-(2′-vinyloxyethoxy)benzaldehyde (1) and malononitrile, and was recrystallized from ethanol. Mp, 117-118°C. ^{1} H NMR (acetone-d_6) δ 3.83 (s, 2 CH_3O-), 3.84-4.43 (m, CH_2= and -O-CH_2-CH_2-O-), 6.23-6.71 (q, =CH-O-), 7.34 (s, aromatic), 8.08 (s, Ph-CH=). IR (KBr) 3112, 3025 (w, =C-H), 2960, 2944, 2918 (m, C-H), 2228 (s, CN), 1655, 1614, 1585, 1573 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 69.92; H 5.42; N, 9.38.

Methyl 3,5-dimethoxy-4-(2′-vinyloxyethoxy)benzylidenecyanoacetate (3)

Compound 3 was prepared according to the literature (16) procedure from 3,5-dimethoxy-4-(2′-vinyloxyethoxy)benzaldehyde (1) and methyl cyanoacetate, and was recrystallized from n-butanol. Mp, 109-110°C. ^{1}H NMR (acetone-d_6) δ 3.82 (s, 3 CH_3O-), 3.84-4.35 (m, CH_2= and -O-CH_2-CH_2-O-), 6.19-6.63 (m, =CH-O-), 7.37 (s,. aromatic), 8.10 (s, Ph-CH=). IR (KBr) 3110, 3024 (m, =C-H), 2958, 2940 (m, C-H), 2220 (s, CN), 1724 (vs, C=O), 1642, 1604, 1577 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{19}NO_6$: C, 61.25; H, 5.75; N, 4.20. Found: C, 61.30; H, 5.72; N, 4.26.

Preparation of 3,4,5-trimethoxybenzylidenemalononitrile **(10)**

3,4,5-Methoxybenzylidenemalononitrile (10) was prepared according to the literature procedure (7) by condensing 3,4,5-trimethoxybenzaldehyde with malononitrile in n-butanol in the presence of piperidine as catalyst. 10: 95%

yield. Mp: 147-148°C. ^{1}H NMR (acetone-d_6) δ 3.85 (s, 3-O-CH_3), 7.33 (s, aromatic 2H), 8.06 (s, Ph-CH=). IR (KBr) 3005 (m, =C-H), 2966, 2932, 2890, 2826 (s, C-H), 2215 (vs, CN), 1590, 1581, 1566 (s, C=C) cm^{-1}.

Preparation of Methyl 3,4,5-trimethoxybenzylidenecyanoacetate (11)

Methyl 3,4,5-trimethoxybenzylidenecyanoacetate (11) was prepared according to the literature procedure (7) by condensing 3,4,5-trimethoxybenzaldehyde with methyl cyanoacetate in n-butanol in the presence of piperidine as catalyst. 11: 88% yield. Mp: 112-113°C. ^{1}H NMR (acetone-d_6) δ 3.84 (s, -O-CH_3), 3.87 (s, 3-OCH_3), 7.43 (s, aromatic 2H), 8.17 (s, Ph-CH=) . IR (KBr) 3115, 3005 (m, =C-H), 2946, 2925, 2835 (s, C-H), 2216 (s, CN), 1732 (vs, C=O), 1599, 1575 (vs, C=C) cm^{-1}.

Radical copolymerizations of 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenemalononitrile (2) *and methyl 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenecyanoacetate* (3) *with ethyl vinyl ether*

In a polymerization tube were placed 0.60 g (2.0 mmol) of **2**, 0.87 g of ethyl vinyl ether (12.0 mmol), 6.57 mg (0.04 mmol) of AIBN, and 0.9 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 solution became gel and stirring magnetic bar stopped. Then polymerization tube was opened and the swelling polymer was poured into 400 mL of diethyl ether. The precipitated polymer was collected and dried under vacum to give 0.67 g (80% yield) of polymer 8; IR (KBr) 3103 (=C-H), 2965, 2938, 2835 (C-H), 2232 (CN), 1637, 1616, 1588 (C=C) cm^{-1}. 9: 91% yield. IR (KBr) 3110 (=C-H), 2938, 2835 (C-H), 2230 (CN), 1742 (C=O), 1635, 1618, 1587 (C=C) cm^{-1}.

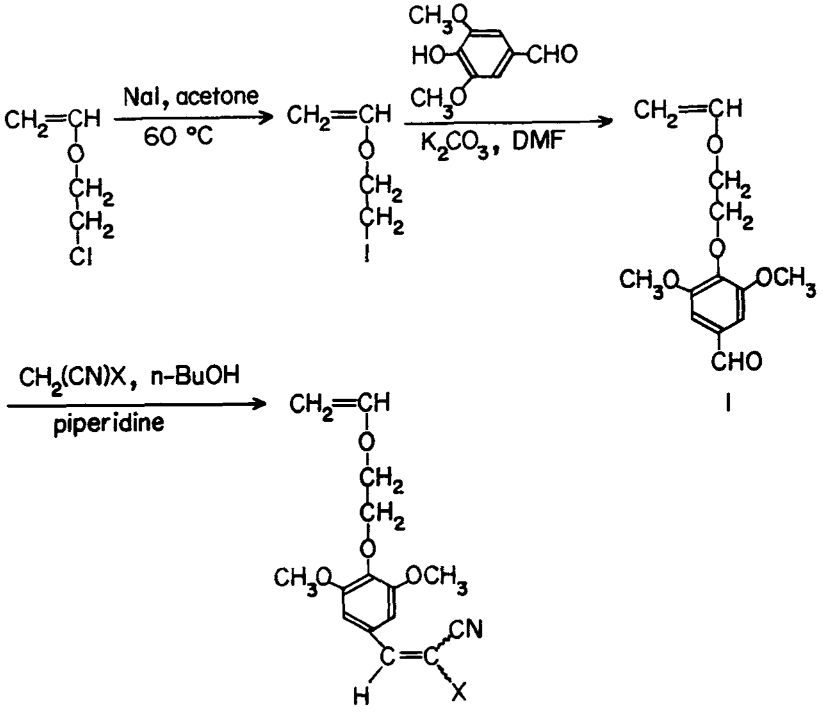
Radical copolymerizations of 3,4,5-trimethoxybenzylidenemalononitrile (10) *and methyl 3,4,5-trimethoxybenzylidenecyanoacetate* (11) *with ethyl vinyl ether*

Model compounds **10** and **11** were polymerized with AIBN according to the literature procedure (16) to give polymers **12** and **13**, and were reprecipitated from acetone into methanol. 12: η_{inh}=0.37 dL/g (c 0.5 g/dL in acetone at 25°C). ^{1}H NMR (acetone-d_6) δ 0.77-1.57 (m, -CH_2- and -CH_3), 1.61-2.24 (m, -Ph-CH-), 2.77-4.01 (m, 3 -OCH_3 and -O-CH_2-), 4.06-4.57 (m, -CH-O-), 5.96-6.37 (m, aromatic 1H), 6.37-6.81 (m, aromatic 1H). IR (KBr) 2958, 2938, 2840 (vs, C-H), 2230 (m, CN), 1582 (vs, C=C) cm^{-1}. Anal. Calcd for$(C_{17}H_{20}N_2O_4)_n$: C, 64.54; H, 6.37; N, 8.85. Found: C, 64.63; H, 6.32; N, 8.90. 13: ^{1}H NMR (acetone-d_6) δ 0.60-1.33 (m, -CH_2- and -CH_3), 1.37-2.17 (m, -Ph-CH-), 2.81-4.07 (m, 4 -OCH_3 and -CH-O-CH_2-), 6.07-6.86 (m, aromatic 2H). IR (KBr) 2950, 2940, 2826 (vs, C-H), 2230 (w, CN), 1742 (vs, C=O), 1586 (vs, C=C) cm^{-1}. Anal. Calcd for $(C_{18}H_{23}NO_6)_n$: C, 61.88; H, 6.63; N, 4.01. Found: C, 61.82; H, 6.58; N, 4.09.

Results and Discussion

Syntheses of monomers 2 *and* 3

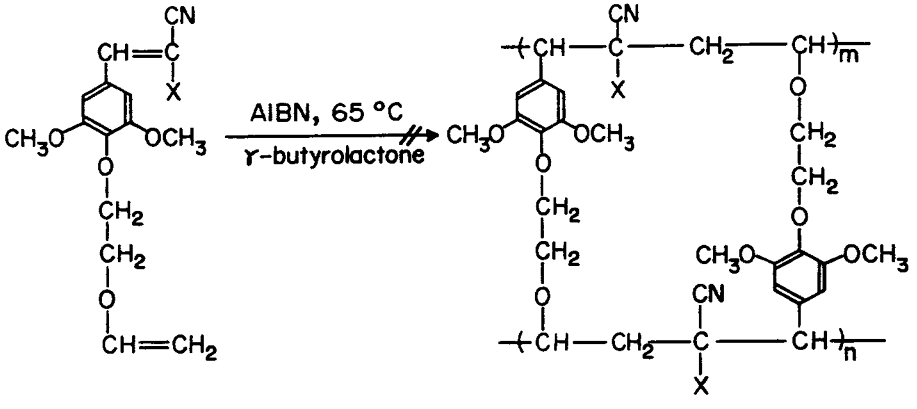
2-Iodoethyl vinyl ether was prepared by the well known halogen exchange reaction (17) from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 3,5-dimethoxy-4-hydroxybenaldehyde to yield 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzaldehyde (1). 3,5-Dimethoxy-4-(2'-vinyloxyethoxy)benzylidenemalononitrile (2) and methyl 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenecyanoacetate (3) were synthesized by the condensation of 1 with malononitrile or methyl cyanoacetate, respectively (18). The chemical structure of the compounds was confirmed by proton-NMR, and IR spectra, and elemental analysis. Spectral data indicated that compound 3 was a mixture of the cis- and trans-isomer.



2, X=CN
3, X=CO$_2$CH$_3$

Radical polymerizations of monomers 2 *and* 3

We have previously prepared p-(2-vinyloxyethoxy)benzylidenemalononitrile and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate, and polymerized by radical initiators to obtain highly crosslinked poly(ethyl vinyl ether)s (16). The polymerizabilities of those bifunctional compounds toward radical initiator were very high and in most cases, polymerized quantitatively by AIBN at 65°C within 3 h. However, 3,5-dimethoxy-4-(2′-vinyloxyethoxy)benzylidenemalononitrile (2) and methyl 3,5-dimethoxy-4-(2′-vinyloxyethoxy)benzylidenecyanoacetate (3) did not polymerize by radical initiators such as AIBN and di-tert-butylperoxide (DTBP) under the same polymerization conditions. All the attempts to homopolymerize 2 and 3 with various radical initiators to secure homopolymer samples (4 and 5) have failed so far. These low polymerizabilities of monomers 2 and 3 toward radical initiators seem to be explained by steric hindrance. Vinyl ether moieties in monomers 2 and 3 are highly crowded by neighboring two methoxy groups, and terminal electron-acceptor groups do not form complexes with electron-donating vinyl ether groups. However, monomers 2 and 3 readily copolymerized with ethyl vinyl ether by radical initiators under the same polymerization conditions. Copolymerizations were carried out in γ-butyrolactone solution at 65°C with AIBN as radical initiator. The copolymerization results are summarized in Table 1. The copolymerizabilities of monomers 2 and 3 toward radical initiators were quite high and in most cases, 2 and 3 copolymerized with ethyl



2, X=CN
3, X=CO_2CH_3

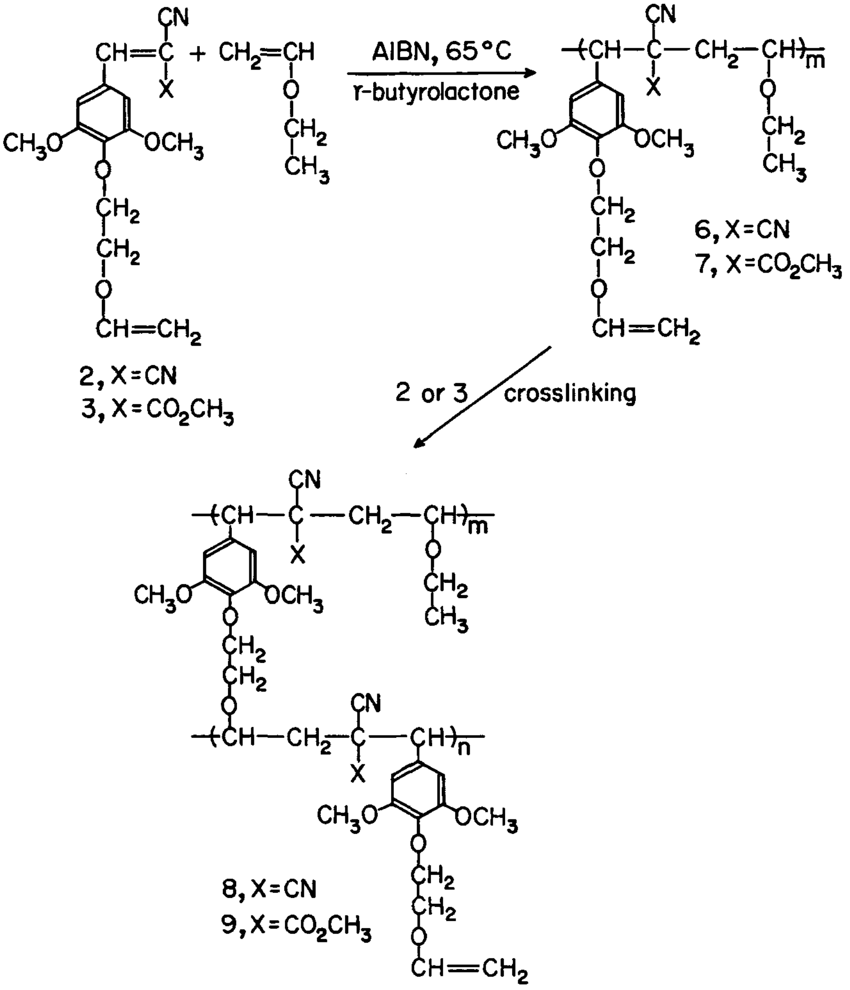
4, X=CN
5, X=CO_2CH_3

Table 1. Free radical polymerizations of 2 and 3 with ethyl vinyl ether by AIBN in γ-butyrolactone at 65°C

Monomer[a] (mol/mol)	Monomer/Solvent (mol/L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
2	2.0	1.5	90	nil
3	2.0	1.5	90	nil
2	2.0	1.2[b]	72	nil
3	2.0	1.2[b]	72	nil
2/EVE, 1/1.0	2.13	1.0	12	75
2/EVE, 1/3.0	1.67	1.0	5	82
2/EVE, 1/6.0	2.15	1.5	3	80
3/EVE, 1/1.0	2.03	1.0	10	78
3/EVE, 1/3.0	1.67	1.0	4	85
3/EVE, 1/6.0	2.03	1.5	3	91

[a] 2 = 3,5-Dimethoxy-4-(2′-vinyloxyethoxy)benzylidenemalononitrile; 3 = Methyl 3,5-dimethoxy-4-(2′-vinyloxyethoxy)benzylidenecyanoacetate; EVE = ethyl vinyl ether. [b] Di-tert-butylperoxide (DTBP) was used as initiator at 120°C.

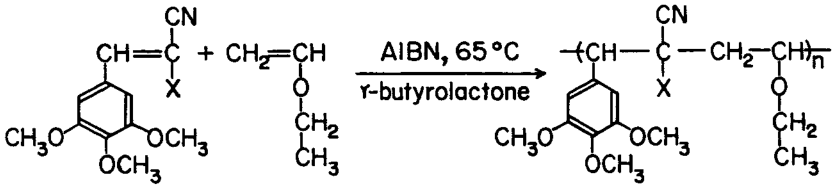
vinyl ether in high yield by AIBN at 65°C within 3 h. The chemical structures of the polymers were identified by IR spectra and elemental analyses. The IR spectra confirmed the chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the copolymers. The trisubstituted terminal double bond participated in the vinyl polymerization, and radical copolymerization of 2 and 3 with ethyl vinyl ether led only to optically trasparent swelling polymers 8 and 9. Radical copolymerizations seem to be proceeded by two reaction steps. In the radical copolymerization depicted in Scheme, the catalyst initiates the polymerization by attacking a initially formed donor-acceptor (EDA) complex, thereby resulting in formation of alternating coplymers 6 and 7 containing pendant vinyl ether groups. The vinyl ether groups of alternating copolymers 6 and 7 again form



EDA complexes with terminal electron acceptors of monomers 2 and 3, thereby resulting to cross-linked copolymers 8 and 9. Polymers 8 and 9 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. Compounds 2 and 3 were also polymerized by cationic initiators to give poly(ethyl vinyl ethers) containing the NLO chromophore 3,5-dimethoxy-4-oxybenzylidenemalononitrile or methyl 3,5-dimethoxy-4-oxybenzylidenecyanoacetate in the side chain, respectively.

Synthesis of model polymers

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 (10) and methyl p-methoxybenzylidene-cyanoacetate (11), 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 10 and 11 copolymerized well with ethyl vinyl ether by



10, X=CN
11, X=CO_2CH_3

12, X=CN
13, X=CO_2CH_3

Table 2. Free radical copolymerizations[a] of 10 and 11 with ethyl vinyl ether by AIBN in γ-butyrolactone at 65°C

Monomer[b] (mol/mol)	Monomer/Solvent (mol/L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)	η_{inh}[c] (dL/g)
10/EVE, 1/1	1.67	0.6	3	92	0.55
10/EVE, 1/2	2.00	0.8	3	95	0.38
10/EVE, 1/3	2.00	1.0	6	96	0.37
11/EVE, 1/1	1.67	0.6	3	88	0.46
11/EVE, 1/2	1.20	0.8	3	90	0.36
11/EVE, 1/3	2.00	1.0	4	94	0.33

[a] The copolymer compositions were estimated to be 1:1 by ^1H NMR spectra and elemental analyses. [b] 10 = 3,4,5-Trimthoxybenzylidenemalononitrile; EVE = ethyl vinyl ether; 11 = methyl 3,4,5-trimethoxybenzylidenecyanoacetate; [c] Inherent viscosity of polymer: 0.5 g/dL in acetone at 25°C.

AIBN as free radical initiator to give high molecular weight (η_{inh}=0.55 dL/g) copolymers **12** and **13** 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 **10** and **11** are strong electron-acceptor olefins and ethyl vinyl ether is a strong electron-donor momoner. The alternating copolymers **12** and **13** were white amorphous materials that were soluble in common organic solvents such as acetone and DMSO. The inherent viscosities of polymers **12** and **13** were in the range of 0.33-0.55 dL/g. Polymers **12** and **13** have good film-forming properties and films cast from acetone solution were cloudy and quite tough.

Properties of polymers

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 **8** and **9** showed a good thermal stability and did not decompose below 290°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 **8** and **9** did not show any characteristic T_g peaks in DSC thermograms. Alternating copolymers **12** and **13** showed a thermal stability up to 290 °C and the T_g values of the polymers were around 163-168°C.

Table 3. Thermal properties of polymers

Polymer	T_g, °C	Degradation temp, °C			Residue at 700°C, %
		5%-loss	20%-loss	40%-loss	
8	-	290	325	352	1.37
9	-	286	325	360	2.35
12	163	286	317	330	0.67
13	168	286	316	316	133

Conclusion

We prepared sterically hindered ethyl vinyl ethers **2** and **3** containing electron acceptors, benzylidenemalononitrile and benzylidenecyanoacetate. Bifunctional monomers **2** and **3** did not polymerize by radical initiators due to the steric hindrance of the vinyl ether groups. These steric hindrance can be overcome by copolymerization, and compounds **2** and **3** copolymerized readily with ethyl vinyl ether by radical initiation. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerization of **2** and **3** with ethyl vinyl ether led to cross-linked polymers **8** and **9**. Model compounds **10** and **11** copolymerized well with ethyl vinyl ether under the polymerization conditions by radical initiators to give 1:1 alternating copolymers **12** and **13** in high yields. Compounds **2** and **3** were also polymerized by cationic initiators to give poly(ethyl vinyl ethers) containing the NLO chromophore in the side chain. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported later.

Acknowledgements

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