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Novel copolymerizations of methyl vinylidene cyanide with electron-rich vinyl monomers

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ABSTRACT

At 28° the spontaneous reactions of methylvinylidene cyanide (MVCN) with p-methoxystyrene, p-trimethylsiloxystyrene, styrene, isobutyl vinyl ether, ethyl vinyl ether and trimethylsilyl vinyl ether yielded alternating copolymers of potential interest as new piezoelectric materials. MVCN copolymerized with vinyl acetate in low yield using radical initiator and $ZnCl_2$. Attempted homopolymerizations of MVCN with various initiators gave only low molecular weight oligomers, particularly trimers.

INTRODUCTION

The copolymer of vinylidene cyanide with vinyl acetate[1] has been shown to be piezoelectric.[2] However, vinylidene cyanide is difficult to prepare and is highly reactive.[1,3,4]

We have found an overlooked monomer in the literature, methyl vinylidene cyanide (MVCN). It is easily synthesized from acetaldehyde and malononitrile.[5]

$$CH_3CHO \quad + \quad CH_2(CN)_2 \xrightarrow{Et_3N} \underset{MVCN}{CH_3CH = C(CN)_2} \quad + \quad H_2O$$

It is significantly less reactive than vinylidene cyanide and is easy to synthesize and store.

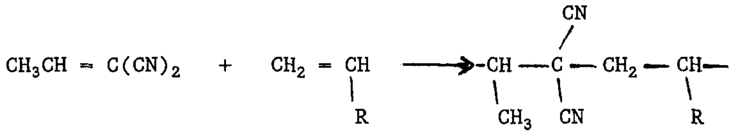
No copolymerization studies of this compound have been reported. We expect that the copolymers of MVCN with vinyl monomers could have interesting piezoelectric, nonlinear optical and other high-technology properties.

The original authors reported that MVCN on standing in contact with basic glass condensed to yellow solids of indefinite structure with molecular weights equal to dimer or less than that of trimer. Therefore, we were also interested to study the possibility of the homopolymerization of MVCN.

RESULTS

Copolymerization

MVCN with p-methoxystyrene, p-trimethylsilyloxystyrene, styrene, isobutyl vinyl ether and ethyl vinyl ether at equimolar feed ratios in bulk spontaneously yielded alternating copolymers (Table 1). Longer reaction times resulted in higher yields. Ultraviolet irradiation using AIBN as photo initiator accelerated these reactions.



$$CH_3CH = C(CN)_2 + CH_2 = \underset{R}{CH} \longrightarrow -\underset{CH_3}{CH}-\overset{CN}{\underset{CN}{C}}-CH_2-\underset{R}{CH}-$$

R = p-methoxyphenyl, p-trimethylsilyloxyphenyl, phenyl, isobutoxy and ethoxy.

Since trimethylsilyl vinyl ether was prepared in THF[6], its copolymerization reaction with MVCN was conducted in this solvent. After 2 days, this solution was not viscous. When AIBN was added and the solution irradiated at 254 nm at 0°C, the solution became very viscous overnight.

With vinyl acetate, bulk spontaneous copolymerization failed even after over one week. Initiation by irradiation of AIBN also failed to form copolymer. However, when AIBN and $ZnCl_2$ were added and the solution irradiated, the copolymer was obtained but in very low yield.

In an attempt to convert co-poly MVCN-poly trimethylsilyl vinyl ether into co-poly MVCN-poly vinyl acetate, the reaction of the former with acetyl chloride in the presence of ZnI_2 was investigated.[7] After 2 days refluxing, 60% of the trimethylsilyl substituents were replaced by acetyl groups, but all the broad peaks of NMR spectrum disappeared. The clear doublet or quartet peaks showed that the polymer had undergone scission by ZnI_2 during the reaction.

Copolymer Properties

The compositions of the copolymer #4, #5 or #6 were 1:1, while #1 or #3 were around 0.45: 0.55 (MVCN:comonomer) by elemental analysis as shown in Table 1. The presence of the methyl substituent in the β position of vinylidene cyanide resulted in somewhat lower Tg's (Table 2) than those of the corresponding VCN polymers. In contrast, literature data [8,9] for the copolymers of styrene with vinylidene cyanide derivatives with bulky β-substituents showed Tg's around 170°C (Table 2).

The Tg of #2 is very low. The bulky trimethylsilyl substituent which is far away from main chain, is "loose" between the polymer chain. But in #6 the bulky silyl group is closer to the main chain, so the decrease of Tg is not so significant.

Oligomerization

MVCN under standard free radical conditions (AIBN, 60°C) did not undergo polymerization. Radical polymerizations were also attempted at room temperature with photoirradiation to overcome a possible low ceiling temperature, but again no viscosity increase was seen.

As to anionic initiators, when $(C_6H_5)_3P$, NaCN or DABCO were used as possible anionic initiators, the bulk polymerizations slowly showed viscosity increase and then turned glassy. Precipitation with methanol gave only traces, but with benzene almost quantitative yields of yellow oligomers, particularly trimer, were formed. These were soluble in acetone or DMSO. The mass spectrum showed a parent ion m/e 276 (trimer).

DISCUSSION

MVCN has shown itself to be an overlooked monomer. Its copolymerization with electron-rich monomers readily gives high yields of high molecular weight copolymers. The gem dicyano group in these copolymers makes them of interest as potential new piezoelectric materials. Their high glass transition temperature and film-forming ability further enhances their possible use in this area.

Table 1: Copolymerization of MVCN with Electron-Rich Vinyl Monomers

	Vinyl Monomer	time (h)	yield (%)	η_{inh} (dl/g)	Tg (°C)	Elemental Analysis C	H	N	wt% of MVCN in copolymer	Mole% of MVCN in copolymer
#1	p-Methoxystyrene	24	80	0.77	190	74.51	6.31	10.91	35	44
#2	p-Trimethylsilyoxy Styrene	172	71	3.22	80	67.43	6.92	8.51	28	45
#3	Styrene	48	73	0.91	165	80.47	6.39	12.30	40	43
#4	Isobutyl Vinyl Ether	24	57	1.65	120	68.76	8.54	14.61	47	51
#5	Ethyl Vinyl Ether	48	54	1.92	120	65.57	7.34	17.03	55	49
#6	Trimethylsilyl Vinyl Ether	10	49	1.75	105	57.67	7.45	12.56	42	48
#7	Vinyl Acetate	10	6	0.31	155	59.88	5.65	14.85	48	46

1. #1, #2, #3, #4 and #5 reaction at bulk at 28°C, #5 in THF and AIBN/hν/0°c, #6 in bulk/0°C and #7 AIBN/$ZnCl_2$/hv.
2. wt% and mole% were calculated from the N analysis.

As to reactivity, this new monomer shows interesting contrast to the parent VCN. Trumbull and coworkers[1] and also Stille and Chung[10] showed that vinyl ethers could not be copolymerized with VCN, because rapid spontaneous initiation leads to mixtures of homopolymers by ionic mechanisms. However MVCN smoothly copolymerizes with vinyl ethers in free radical fashion.

A second interesting contrast is found with vinyl acetate: VCN smoothly copolymerizes with VOAC, but MVCN does so only reluctantly and with the aid of $ZnCl_2$. The Lewis acid complexes with the CN groups to make MVCN more electrophilic.

These differences can be explained in terms of our Bond-Forming Initiation theory.[11] MVCN is a less electron-poor olefin than the parent VCN due to the β-methyl group. This results in a shift to free radical spontaneous polymerization with styrenes.

In the reaction of co-poly-MVCN-poly-trimethylsilyl vinyl ether with acetyl chloride and ZnI_2, the scissioning of the polymer may be due to the coordination of the cyano group with the very electrophilic complex, CH_3COCl/ZnI_2, which enhances the polymer bond breaking.

These copolymers' piezoelectric properties are currently being evaluated.

EXPERIMENTAL

Instrumentation

^1H NMR and ^{13}C NMR spectra were taken on a Brucker WM 250 nuclear magnetic resonance spectrometer at 250 MHz. Infrared spectra were recorded on Perkin-Elmer 983 spectrometer. Elemental analysis were performed by Desert Analytics, Tucson, AZ. Satisfactory analytical data (± 0.3% for C, H, and N) were obtained.

Materials

Trimethylsilyl vinyl ether was prepared according to the literature.[6] p-Methoxystyrene, styrene, isobutyl vinyl ether, ethyl vinyl and vinyl acetate were purchased from Aldrich and distilled from calcium hydride.

Preparation of MVCN[5]

MVCN was prepared according to the general procedure for Knoevenagel condensation. Malononitrile (33g, 0.5 mole) and acetaldehyde (30g, 0.7 mole) were dissolved in 500ml of benzene, and a few drops of diethylamine were added. The solution was left at room temperature for 2 hours, and then washed with dilute hydrochloric acid and water, and dried over Drierite. Removal of the solvent gave a clear liquid, which was vacuum distilled from glassware which was previously washed with dilute hydrochloric acid. B.P. 39-40°C/0.2torr, yield 65%, d=0.914, NMR (CCl_4): δ 7.75 (quart,1H), 2.25 (d, 3H).

General Procedure for the Spontaneous Polymerization

Spontaneous polymerization reactions were carried out under argon atmosphere in Pyrex polymerization tubes with high vacuum valves. The polymers were precipitated by methanol.

General Procedure for the Photochemical Reactions in the Presence of AIBN

Polymerizations were carried out in the quartz tube using high pressure Mercury lamp (50W). The products were precipitated by methanol.

Reaction of MVCN with Bases

MVCN was mixed with various bases. After several days, the mixtures were glassy. The products were recrystallized from methanol, gave a pale-

Table 2: Comparison of Tg of Copolymers from VCN or MVCN (M_1) with Vinyl Monomers (M_2)

M_1	M_2	tg(°C)
VCN	VA	180[a]
MVCN	VA	155
VCN	St	180-190[a]
MVCN	St	165
3-Phenyl VCN	St	120-130[b]
3-Cyclohexenyl-VCN	St	175[c]
5-Norbornenyl-VCN	St	170[c]
1-Naphthyl-VCN	St	185[c]
3-Pyridinyl-VCN	St	175[c]

VCN = Vinylidene cyanide, VA = vinyl acetate, St = styrene.

a. Ref 4. b. Ref. 8 c. Ref. 9

yellow powder, m.p. 180-187°C, yield 87%. ^{1}H NMR (acetone): δ 1.5 (d,3H), 1.85 (d,3H), 2.5(m 1H), 2.6 (m,1H), 3.4-3.6 (m 3H), 5.2 (d.1H). ^{13}C NMR (acetone): δ 102, 103, 104, 105, 106, 107 (CN), 38, 35, 30, 23, 20, 12, 10ppm. MS: m/e = 276 ($M^{+\cdot}$).

Reaction of Co-poly-MVCN-Trimethylsilyl Vinyl Ether with ZnI_2 and CH_3COCl

Copolymer (contained 0.05 mol of $-OSiMe_3$), zinc iodide (0.05 mol) and acetyl chloride (0.05 mol) were mixed with 1,2-dichloroethane (80 ml) and dry ether (20 ml), and the mixture was refluxed for overnight. The solvents were removed. The residue was extracted by dry chloroform. The chloroform solution was then investigated with NMR spectroscopy, which showed depolymerization had taken place.

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