Spontaneous Copolymerization of Alkoxyallenes with Aryl Isocyanates through Zwitterionic Intermediates

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ABSTRACT: Alkoxyallene (1) and aryl isocyanates (2) underwent spontaneous copolymerization at 80 °C to obtain a polyamide consisting of three type of units, accompanying the typical formation of β-propiolactam derivatives. The behavior of the copolymerization was dependent on reaction conditions (solvent and monomer feed ratio) and/or the electron-withdrawing capacity of the para substituent of aryl isocyanates. Especially, copolymerization of 1 with the more electrophilic 4-chlorophenyl isocyanate yielded an alternating copolymer. It might be suggested that the spontaneous copolymerization of 1 and 2 would proceed through zwitterionic intermediates generated from 1 and 2.

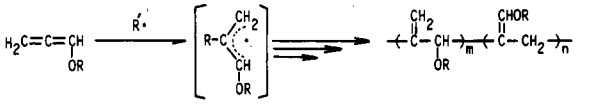
Introduction

Allene derivatives have attracted little attention as polymerizable monomers in spite of their simple structure in which another perpendicular methylene carbon is bonded to the corresponding vinyl monomers. We have been engaged in a systematic study of polymerization of the substituted allenes in comparison with the corresponding vinyl monomers. Our results showed that substituted allenes have good ability and novel character in radical polymerization (Scheme I).[1]

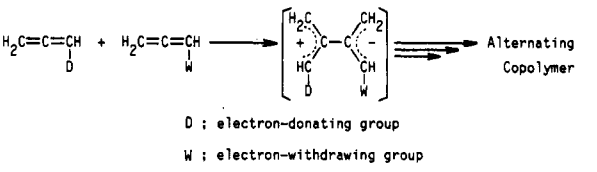
The spontaneous copolymerizations of nucleophilic and electrophilic vinyl monomers have been widely investigated and given a new important position on several aspects of mechanistic and material chemistry.[2] Recently, we first reported the spontaneous copolymerization of alkoxyallene with electrophilic cumulated double-bond systems and demonstrated that alkoxyallenes have higher nucleophilicity toward electrophiles than the corresponding vinyl ethers because the spontaneous reaction can proceed through stable allyl-type zwitterionic intermediates to yield alternating copolymers (Scheme II).[3]

As a part of our survey of the zwitterionic reaction of allene derivatives, it is important to evaluate the copolymerizability of nucleophilic allenes with electrophilic *hetero*cumulenes. Thus, we now report copolymerization behavior of methoxyallene (1) with para-substituted phenyl isocyanates (2).

Scheme I



Scheme II



Experimental Section

Infrared (IR) spectra were recorded with a Jasco FT/IR-3 spectrometer and are presented (cm^{-1}) for key absorption. ^1H NMR spectra were taken with JEOL PMX-60 and JEOL FX-100 spectrometers with tetramethylsilane (TMS) as internal standard; chemical shifts are expressed in δ values. ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer. Mass spectra were recorded on a Hitachi M-80 GC–MS. Composition of polymer was estimated by elemental analysis (Yanaco CHN corder MT-2) or ^1H NMR (integral ratio of aromatic protons to other protons). The average molecular weight of the obtained polymers was estimated by gel permeation chromatographic analysis (GPC; solvent, tetrahydrofuran at 35 °C) with Toso HPLC CCP & 8000 system equipped with three polystyrene gel columns (TSK gel, G-2000HXL, G-2500HXL, and G-3000HXL or G-2000HXL, G-5000HXL, and G-4000HXL).

Materials. 1-Methoxy-1,2-propadiene (1) was prepared by isomerization of 1-methoxyprop-2-yne with a catalytic amount of potassium *tert*-butoxide according to the reported procedure.[4] Para-substituted phenyl isocyanates (**2a**, X = Me; **2b**, X = H; and **2c**, X = Cl) were all of commercial grade and purified by distillation under reduced pressure from CaH_2 or recrystallization from dry benzene. All of the polymerization solvents were distilled and stored with metallic sodium or 4A molecular sieves.

Copolymerization. The typical procedure was carried out as follows. In a glass tube, 1 (0.70 g, 10.0 mmol) and **2c** (1.54 g, 10.0 mmol) were placed. The tube was degassed and sealed in vacuo and then placed in a constant-temperature bath. The reaction mixture was stirred for 24 h at 80 °C. The tube was then opened, and conversion of **2c** was estimated by measuring the decrease of the isocyanate concentration by GC. The resulting viscous oil was dissolved in Et_2O. After filtration, the ether solution was poured into a large volume of hexane. The precipitated white polymer was collected and dried in vacuo (0.49 g, 22% yield): IR (KBr) 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–6.5 (aromatic, 4 H), 6.2–4.8 (C=CH– and $C=CH_2$), and 4.0–2.9 (OCH_3, CH_2, CH).

Cycloadduct of 1 with 2c. After filtration of polymer from 1 (0.70 g, 10.0 mmol) and **2c** (1.54 g, 10.0 mmol), the filtrate was concentrated to yield viscous oil (1.59 g). By column chromatography of the resulting oil using silica gel (Wacogel C-200) with cosolvent of ethyl acetate and hexane, *N*-(4-chlorophenyl)-3-methylene-4-methoxy-2-azetidinone (**3a**) (0.19 g, 12%) was obtained: IR (neat) 1760 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70–7.10 (m, 4 H), 5.95–5.75 (m, 2 H), 5.45–5.35 (m, 1 H), 3.25 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 159.8, 145.3, 136.0, 130.0, 129.4, 118.0, 113.7, 86.6, 49.7; MS (*m/e*) 223 (M^+). **3b**: ^1H NMR ($CDCl_3$) δ 7.70–7.10 (m, 4 H), 3.67 (s, 2 H), 3.47 and 3.37 (2s, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.9, 145.2, 136.4, 129.2, 129.0, 119.9, 118.3, 77.2, 52.4.

Results

Copolymerization of 1 with 2. The reactions of an equimolar mixture of methoxyallene (1) and some 4-substituted phenyl isocyanates (**2a**, X = Me; **2b**, X = H; **2c**, X = Cl) were carried out at 80 °C in bulk without initiators to obtain the corresponding copolymers. All obtained copolymers were soluble in Et_2O, although each homopolymer of 1 or 2 was insoluble in Et_2O. Their compositions

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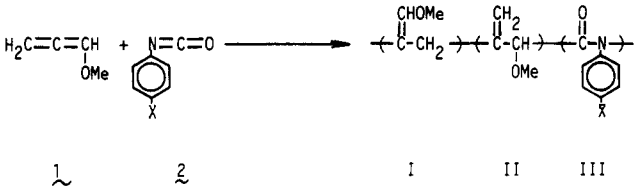
Table I
Reaction of 1 with Aryl Isocyanate[a]

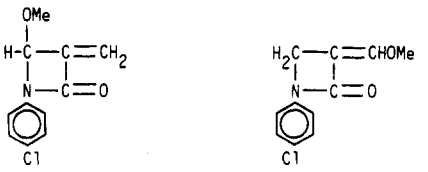
entry	isocyanate	conv,[b]	yield,[c] %	$\bar{M}_n$[d]	composition[e] I	II	III
1	**2a**	26	8	800	62	12	26
2	**2b**	63	16	4400	59	5	36
3	**2c**	82	22	900	25	27	48

[a] Reacted at 80 °C for 24 h in bulk. [b] Measured by GC. [c] Insoluble in methanol. [d] Estimated by GPC (based on PSt). [e] Estimated by ^{1}H NMR analysis.

Scheme III



Scheme IV



and molecular weights were estimated by ^{1}H NMR and GPC, respectively (Table I). The proportion of the units derived from **2** was also evaluated by elemental analysis and consistent with the value calculated by ^{1}H NMR.

The reaction was found to be faster with increasing electrophilicity of **2**. Namely, 82% of 4-chlorophenyl isocyanate (**2c**) reacted with **1**, whereas only 26% of 4-methylphenyl isocyanate (**2a**) was consumed under the same conditions (24 h, 80 °C) (entry 3 vs 1). The proportion of the units derived from **1** also decreased with increasing electrophilicity of **2**.

The typical spectral feature of all copolymers was a strong band of an amide group[6] at 1710 cm^{-1} in the IR spectra, and the ^{1}H NMR spectra of the copolymers showed the signals assignable to the olefinic protons of the vinyl ether group and of the *exo*-methylene group at 6.2–5.5 and 5.3–4.8 ppm, respectively; this supported the assumption that **1** was polymerized by respective 1,2- and 2,3-double bonds, similarly to the radical polymerization of **1** (Scheme III).[1]

Furthermore, in the ^{1}H NMR spectra of the copolymer of **1** and **2c**, the absence of signals at 3.0–2.0 ppm due to the >C–CH_2–C< group of the homopolymer of **1** implied that the copolymer with **2c** contained no homopolymer unit from **1**. In addition, from the hexane-soluble part, a cycloadduct (**3a**) was isolated in 12% yield and another isomer (**3b**) was identified by ^{1}H NMR in the mixture of **3a** and **3b** (Scheme IV). The reaction of alkylallenes and chlorosulfonyl isocyanate, a more electrophilic heterocumulene, has been reported to afford the corresponding β-propiolactam derivatives through zwitterionic intermediates.[5]

The isolated β-lactam derivatives did not react with excess **1** to yield polymer even at higher temperature. Therefore, the possible initiation of the copolymerization by thermal decomposition of **3** was excluded.

Copolymerization of 1 with 2c. Copolymerization of **1** with **2c** was further carried out under some different conditions which are summarized in Table II, since a 1:1 copolymer of **1** and **2c** was obtained even in bulk. The molecular weight of the obtained copolymer was estimated by GPC based on polystyrene. The hexane-soluble part contained oligomers, the structure of which was the same as that of the hexane-insoluble polymer.

Table II
Copolymerization of 1 with 2c[a]

entry	solvent	feed, 1/2c	time, h	yield, % A[b]	B[c]	$\bar{M}_n$[d]	composition[e] I	II	III
1	$MeNO_2$[f]	1	24	5	3	900	27	21	52
2	DCE[g]	1	24	6	54	700	43	7	50
3	DMF[h]	1	24	0	0				
4	MeCN[i]	1	24	24	46	1300	23	26	51
5	MeCN	0.33	24	7	26	1100	27	25	48
6	MeCN	3	24	14	47	1200	(68)		32
7	MeCN	1	12	6	14	800			
8	MeCN	1	72	13	45	1100	24	24	52

[a] Copolymerized at 80 °C, [total monomer] = 1 mol/L. [b] Polymer insoluble in methanol. [c] Dimer and oligomer soluble in methanol. [d] Estimated by GPC (based on PSt). [e] Estimated by ^{1}H NMR analysis. [f] Nitromethane. [g] 1,2-Dichloroethane. [h] *N,N*-Dimethylformamide. [i] Acetonitrile.

As shown in Table II, the yield of copolymer increased in *n*-donor solvents such as acetonitrile except for *N,N*-dimethylformamide (DMF). In DMF, the reaction of **1** and **2c** gave not copolymer at all but a cyclotrimer of **2c**, isocyanurate, which was identified by authentic sample,[7] even though DMF had been reported to be a suitable solvent for copolymerization through zwitterionic intermediates.[8] Furthermore, the obtained polymers were always 1:1 copolymers independent of solvents.

Further, we attempted to clarify other factors on successful copolymerization in acetonitrile. Entries 4–6 showed the change of copolymer composition with varying monomer feed ratio. When the mole fraction of **1** in monomer mixture is 75%, the copolymer contained more than 50 mol % of **1**. In contrast, the spontaneous reaction of **1** with cyanoallene afforded a 1:1 copolymer irrespective of the monomer feed ratio.

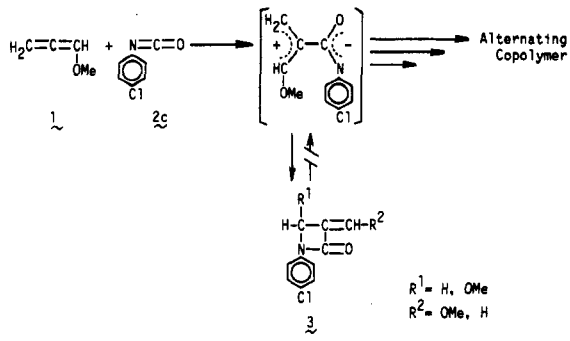
The yield and the molecular weight of the copolymer increased with the reaction time up to 24 h with little accompanying change of the polymer composition. After 24 h, however, the yield and the molecular weight did not increase.

Discussion

We discuss all these results in terms of our reported spontaneous copolymerization mechanism through an allyl-type stable zwitterionic intermediate. The proposed pathway was suggested by the isolation of β-propiolactam derivatives **3** because similar β-propiolactams were reported to be formed by the intramolecular ring closing of a zwitterion generated from alkylallenes and chlorosulfonyl isocyanate.[4] Furthermore, the obtained lactam could not open back to a zwitterion, which can initiate the cationic homopolymerization of **1** (Scheme V).

The copolymerizability of **2** was dependent on their electrophilicity. When the electrophilicity of aryl isocyanate was weak, the rate of formation of a zwitterion would become slow and the allyl cation end-group of the zwitterion would react not only with the allyl anion end-group of the zwitterion to yield an alternating copolymer but also with free methoxyallene to produce a copolymer containing more than 50 mol % of methoxyallene units. However, it was confirmed that the copolymer of **1** and **2c** had an alternating structure because of the absence of homopolymer units of **1** and the formation of cycload-

Scheme V



ducts of the zwitterionic intermediates from 1 and **2c** in higher yield.

The reaction solvents did not affect the composition of the resulting copolymers with **2c** but influenced the yield of copolymers. This effect of reaction solvents also indicated that the polymerization proceeded through ionic intermediates. On the other hand, when the mole fraction of 1 in the monomer feed ratio was greater than 50 mol %, the copolymer contained more than 50 mol % of methoxyallene units. In this condition, it appeared that the cationic homopolymerization of 1 was initiated by the generated zwitterion, competing with copolymerization through polycombination of one. Furthermore, the yield and the molecular weight of the copolymer increased with time up to 24 h, but after 24 h the molecular weight did not increase, indicating that the termination reaction on the generated zwitterion occurred faster than that of the reaction of 1 with cyanoallene.[3]

Conclusions

In this work, we found the spontaneous copolymerization of methoxyallene and aryl isocyanates through zwitterionic mechanism and studied the effects of reaction conditions on the polymerization behavior. We have concluded that (i) the reactivity of aryl isocyanates was dependent on the electron-withdrawing capacity of para substituents, and an alternating copolymer was obtained by using 4-chlorophenyl isocyanate; (ii) *n*-donor solvent such as acetonitrile was suitable for the copolymerization of 1 and **2c**, and the copolymer composition was dependent on the monomer feed ratio, contrary to the copolymerization of 1 and cyanoallene; (iii) the polymerization course through a zwitterion was suggested by the formation of β-propiolactam derivatives as intramolecular cycloadducts of the zwitterion.

References and Notes

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Registry No. 1, 13169-00-1; (1)(**2a**) (copolymer), 132622-57-2; (1)(**2b**) (copolymer), 132622-58-3; (1)(**2c**) (copolymer), 132622-56-1; **2c**, 104-12-1; **3a**, 121280-57-7; **3b**, 132622-52-7.