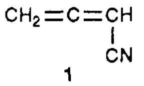
Communications to the Editor

A New Cross-Linking Method Involving Zwitterions. Reaction of Polymers Containing Allenyl Ether Moieties with Electrophilic Cumulenes

Introduction. Cross-linking of polymers plays an important role in the field of material science. A number of different procedures have been used, e.g., cationic and anionic ring-opening reactions of reactive functions such as epoxides,[1] radical additions of dithiols to carbon–carbon double bonds,[2] additions of alcohol or amino groups to diisocyanates,[3] and condensations of dialdehydes with amino groups,[4] etc. In all these cases, each cross-link is formed via reaction of reactive functional groups in the two polymer chains. If a reactive group in the polymer could be converted into a zwitterion, two bonds between the polymers would be formed simultaneously, and a higher density of cross-linking would be expected (Scheme I). Furthermore, a monofunctional species could be used as a cross-linking reagent in zwitterionic cross-linking, in contrast to multifunctional compounds such as diisocyanates and diols required for standard cross-linking procedures.

Recently, we have reported the spontaneous copolymerization of alkoxyallenes with cyanoallene[5] or isocyanate[6] via a zwitterionic mechanism. This paper describes the first example of a zwitterionic cross-linking of a polymer having an allenyl ether group with cyanoallene (1) or 4-chlorophenyl isocyanate (2) cross-linking reagents.



$CH_2{=}C{=}\underset{CN}{CH}$

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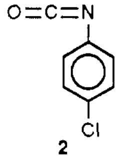

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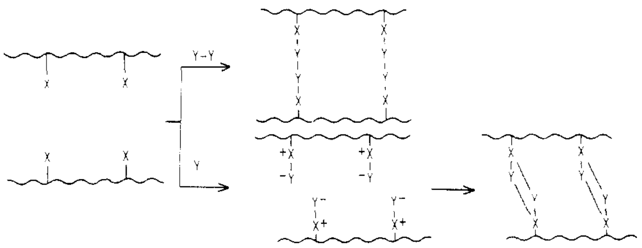
Experimental Section. Materials. Commercially available 4-chlorophenyl isocyanate (2) was purified by recrystallization from dry benzene. All of the reaction solvents were distilled and stored with metallic sodium or 4A molecular sieves.

Cyanoallene (1). 1 was prepared according to the following procedure.[7] To a suspension of propargyl bromide (70.00 g, 0.59 mol), copper(I) cyanide (5.80 g, 65 mmol), and water (5.9 mL) was added dropwise a solution of potassium cyanide (41.25 g, 0.74 mol) in water (73.5 mL) at 60 °C, and the resulting mixture was stirred for 30 min. After cooling, the reaction solution was extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated. The residue was purified by distillation to give 1 (21.61 g, 56% yield): bp 20–35 °C (15 Torr).

4-[(Allenyloxy)methyl]styrene (3). 4-[(Propargyloxy)methyl]styrene (4.00 g, 23.3 mmol), prepared by etherification of propargyl alcohol with 4-(chloromethyl)styrene, was added slowly to a THF solution of potassium *tert*-butoxide (0.65 g, 5.8 mmol) and reacted at 0 °C for 1 h. The reaction mixture was poured into ice–water, followed by extraction with ether. After removal of the solvent in vacuo, the residual oil was distilled to give 3 (1.90 g, 48% yield): bp 65 °C (10 Torr); IR (neat) 1945, 1624, 1195, 900, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.30 (s, 4 H, aromatic), 6.78 (t, J = 6.0 Hz, 1 H, $=C=CH-$), 6.67 (dd, J = 17.8 and 10.6 Hz, 1 H, $=CH-$), 5.67 (dd, J = 17.8 and 1.2 Hz, 1 H, $H_2C=$), 5.42 (d, J = 6.0 Hz, 2 H, $CH_2=C=$), 5.18 (dd, J = 10.6 and 1.2 Hz, 1 H, $H_2C=$), 4.57 (s, 2 H, $-CH_2O-$); ^{13}C NMR ($CDCl_3$) δ 201.3, 137.1, 136.8, 136.4, 128.0, 121.5, 113.9, 91.1, 70.3. Anal. Calcd for $C_{12}H_{12}O$: C, 83.60; H, 7.02. Found: C, 83.17; H, 6.92.

Scheme I



Copolymerization of 3 with Styrene. A typical procedure was carried out as follows: A benzene (7.7 mL) solution of 3 (0.40 g, 4.5 mmol), styrene (2.18 g, 40.5 mmol), and azobis(isobutyronitrile) (0.19 g, 5 mol %) were placed in a glass tube. The tube was degassed, sealed in vacuo, and then placed in a constant-temperature bath. After the reaction mixture was stirred for 24 h at 60 °C, the tube was opened and the resulting viscous oil was dissolved in dichloromethane and precipitated by pouring the solution into a large volume of methanol. The precipitated white polymer was collected and dried under reduced pressure. The copolymer composition was estimated by ^{1}H NMR analysis based on the relative intensities of the signals at δ 8.0–5.0 (aromatic protons and $-CH=C=$) and 5.4 ($=C=CH_2$) ppm: IR (KBr) 3030, 3000, 2900, 2820, 1945, 1595, 1485, 1440, 1180, 1030, 750, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.0–6.1 (aromatic), 5.4 ($=C=CH_2$), 4.5 ($-OCH_2-$), 2.5–0.8 ($-CH_2-$, $-CH-$).

Cross-Linking of the Copolymer with Cumulenes. A typical procedure was carried out as follows: A dichloromethane (0.4 mL) solution of the copolymer (St:3 = 91:9) (100 mg) and 1 (5 mg, 0.08 mmol: an equimolar quantity to the allenyl ether moieties of the copolymer) were placed in a tube, which was degassed, sealed in vacuo, and then placed in a constant-temperature bath. After reaction, the gelled polymer was washed with acetone and dried under reduced pressure.

Analytical Methods. Molecular weight and molecular weight dispersion were measured by Toyo Soda HPLC CCP&8000 using TSK gel G-2000HXL, G-2500HXL, and G-3000HXL (solvent, THF). IR spectra were recorded on a JEOL FT/IR-3 spectrometer, and NMR spectra were obtained by JEOL PMX-60 (60 MHz) and FX-100 (100 MHz) spectrometers.

Results and Discussion. Synthesis and Polymerization of 3. In order to prepare a polymer having an allenyl ether group, we designed the synthesis and polymerization of 4-[(allenyloxy)methyl]styrene (3), which has both an allenyl ether and a vinyl group. In a previously reported method,[8] 3 was prepared at 0 °C by isomerization of the corresponding propargyl ether [4-[(propargyloxy)methyl]styrene] in the presence of a catalytic

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Table I
Copolymerization of 3 with St[a]

monomer feed ratio (3:St)	yield,[b] %	$\bar{M}_n$[c]	copolym composn[d] 3:St
20:80	65[e]		
10:90	75	8520	9:91
5:95	63	6040	5:95

[a] Polymerized at 60 °C for 24 h in benzene. [b] Insoluble polymer in methanol. [c] GPC (based on PSt). [d] Estimated by ^{1}H NMR. [e] Cross-linked during precipitation.

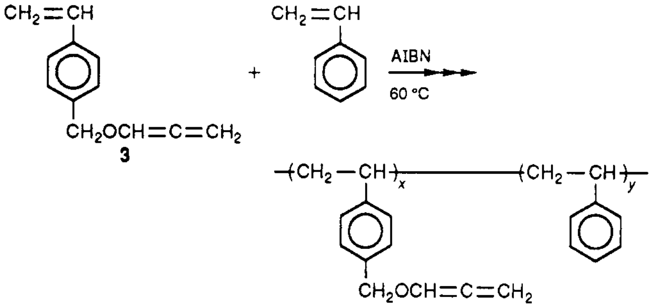
Table II
Cross-Linking Reaction of Copolymers with 1 or 2[a]

copolym composn (3:St)	cross-linking agent	temp, °C	gelation time, min
9:91	1	60	1
	1	20	180
	2	80	120
5:95	1	60	60
	2	80	120
9:91		60	>52 h

[a] Cross-linking agent: 1, cyanoallene; 2, 4-chlorophenyl isocyanate. Reacted with an equimolar quantity to the allenyl ether moiety of 3.

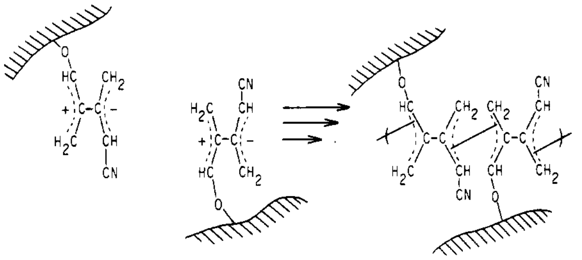
amount of potassium *tert*-butoxide. The allenyl ether 3 was obtained in 48% yield as colorless oil after distillation [bp 65 °C (10 Torr)], and the structure of 3 was confirmed by elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectra.

Copolymerizations of 3 with styrene (St) were carried out with azobis(isobutyronitrile) (AIBN) in benzene at 60 °C to obtain soluble copolymers containing less than 10 mol % of 3 (Table I). The ^{1}H NMR spectra of the copolymers indicated a signal corresponding to the terminal proton of the allenyl ether group at 5.4 ppm, and IR spectra also showed a characteristic allenic absorption at 1945 cm^{-1} similar to that for monomeric alkoxyallenes. These data demonstrated that the radical copolymerization of 3 with St could proceed only through the vinyl group of 3 to give a soluble polymer having the desired allenyl ether group.



Cross-Linking by Cumulenes. The reactions of copolymers with 1 or 2 were investigated, and the results are shown in Table II. Blank experiments without 1 or 2 indicated that the copolymers were not affected by heating. However, the copolymers were readily cross-linked by an addition of either 1 or 2, although the cross-linking reaction was slower with 2.

Scheme II



IR spectra of the polymers cross-linked with 1 showed new broad absorption bands at 1660–1620 cm^{-1} (olefinic moiety) and 2220 cm^{-1} (cyano group) similar to those observed in copolymers obtained from methoxyallene and 1.[5] Further, IR spectra of the polymers cross-linked with 2 showed a characteristic absorption of a trisubstituted amide group at 1720–1740 cm^{-1} also found in copolymers of methoxyallene and 2.[6] In addition, the absorption of the allenyl ether group at 1945 cm^{-1} disappeared completely in both cases. These observations are consistent with a cross-linking reaction occurring by coupling between zwitterions generated on different polymer chains as depicted in Scheme II. The carbon–carbon bond between the central carbon of the nucleophilic allenyl ether group on the polymer chain and that of the electrophilic cumulated double bond of 1 or 2 was formed first, followed by the cross-linking reaction.

This is the first known example of a zwitterionic cross-linking reaction of a polymer having an allenyl ether group such as those in 1 and 2. We propose that this new concept of cross-linking method is applicable to a variety of zwitterionic polymerization systems.

References and Notes

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