Polyaddition of Diallenes: Radical Polyaddition of Dithiols to 1,4-Bis(allenyloxy)benzene

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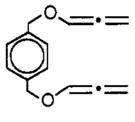
Received February 16, 1993; Revised Manuscript Received June 22, 1993[●]

ABSTRACT: A new diallene, 1,4-bis(allenyloxy)benzene (2), was synthesized and its radical polyadditions of dithiols such as 1,4-benzenedithiol or bis(4-mercaptophenyl) sulfide to the diallene were carried out. The diallene was prepared in a one pot reaction from hydroquinone and propargyl bromide with 3.0 equiv of *tert*-butoxide in dimethyl sulfoxide. The polyaddition was carried out at 60 °C in the presence of 2,2′-azobis(isobutyronitrile) as an initiator to afford soluble polymer containing both reactive carbon–carbon double bonds in the main chain and methyl groups in the side chain in high yield. This polymer structure could be confirmed to be formed by selective attack of thiyl radical to the center carbon of the allenyl group, followed by abstraction of the hydrogen of the thiol group at the terminal carbon of the allenyl group. The obtained polymer easily underwent cross-linking by the reaction of the double bonds in the backbone with Lewis acid at ambient temperature.

Introduction

Selective polymerization of one of the two carbon–carbon double bonds of allene derivatives may be expected as a useful method to synthesize functional polymers containing double bonds by a simple procedure. For example, radical,[1] cationic,[2] and zwitterionic polymerization[3] of allene derivatives such as alkoxyallene and phenylallene afford functional polymers having carbon–carbon double bonds *in the side chain.* We have recently reported the synthesis of another type of allene polymer containing double bonds *in the backbone* by the radical polyaddition of dithiols to 1,4-bis(allenyloxy)xylylene (1) and demonstrated that the polymers easily undergo cross-linking by the reaction of double bonds in the backbone with Lewis acid.[4] This paper involves an extension of this work by using a newly prepared diallene, 1,4-bis(allenyloxy)benzene (2). The polymer from 2 will be expected to be thermally more stable than that from 1, because the polymer from 2 does not have benzylic methylene groups which are liable to undergo oxidative degradation at higher temperature.



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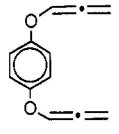

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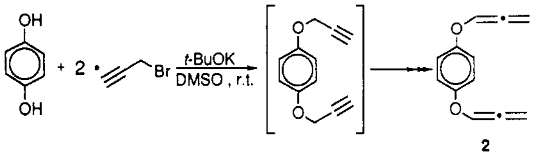
Results and Discussion

Initially, the requisite diallene 2 was prepared using a two-step reaction analogous to the method reported for monofunctional alkoxyallenes:[5] preparation of the corresponding propargyl ether from hydroquinone and propargyl bromide in the presence of sodium hydroxide, followed by isomerization of the ether to 2 with a catalytic amount of potassium *tert*-butoxide in tetrahydrofuran (THF). However, the overall yield was only 10%. Accordingly, the reaction was effected in one pot reaction from hydroquinone and propargyl bromide with 3.0 equiv of *tert*-butoxide in dimethyl sulfoxide (DMSO) to improve the overall yield up to 65%.

Table I. Radical Polyaddition of Dithiols to 2[a]

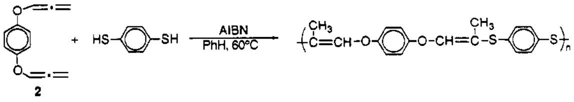
entry	R	time/h	Y/%	$\bar{M}_n$[b]	E/Z[c]
1	BDT	3	94	1500	39/61
2	BDT	6	93	2600	24/76
3	BDT	12	95	3800	19/81
4	BDT	24	95	6400	15/85
5	BDT	48	97	8200	12/88
6	MPS	3	89	2500	38/62
7	MPS	6	94	3800	25/75
8	MPS	12	96	5400	27/73
9	MPS	24	95	8100	12/88
10	MPS	48	94	9900	11/89

[a] The polyaddition was carried out at 60 °C with AIBN (3 mol %) in benzene (2.5 mol/L). [b] Estimated by GPC based on PSt. [c] Estimated by ^{1}H NMR.



(1)

Radical polyadditions of aromatic dithiols such as 1,4-benzenedithiol (BDT) and bis(4-mercaptophenyl) sulfide (MPS) to 2 were carried out at 60 °C with 2,2′-azobis(isobutyronitrile) (AIBN) as a radical initiator in benzene in a sealed tube under reduced pressure.[6] The results are summarized in Table I. In both polyadditions of BDT and MPS to 2, polymer yields are almost quantitative irrespective of reaction time, whereas their average molecular weights increase with time, indicating that the polymerization proceeds via polyaddition without serious side reactions. All of the polymers obtained here were soluble in benzene, dichloromethane, chloroform, THF, etc. The methyl groups in the side chain contribute to the high solubility since unsubstituted olefin containing polymers obtained by a similar radical polyaddition of dithiols to diynes are generally insoluble in common organic solvent.[7]



(2)

The IR spectra of the polymers showed the characteristic absorptions of trisubstituted carbon–carbon double bonds at 1641 and 815 cm^{-1}, and an absorption attributable to a vinyl ether group at 1207 cm^{-1}. Figure 1 shows the ^{1}H NMR spectrum of the polymer measured in C_6D_6. The

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[●] Abstract published in *Advance ACS Abstracts,* August 15, 1993.

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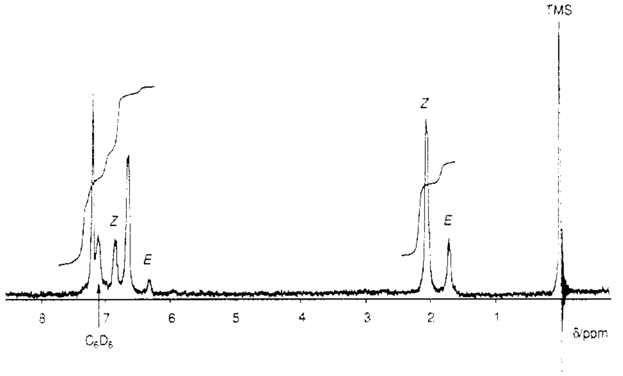
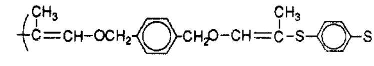
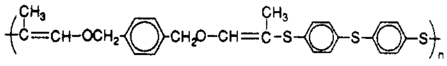
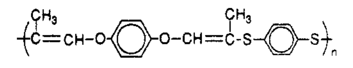
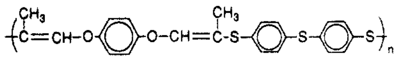


Figure 1. 60-MHz ^{1}H NMR spectrum of the polymer obtained from 2 and BDT in C_6D_6.

Table II. Thermal Stability of Polymer[a]

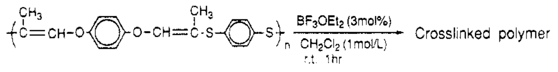
polymer	$\bar{M}_n$[b]	$T_{10\%}$, °C[c]
	6000	243
	5900	281
	6400	306
	5400	312

[a] Thermogravimetric analysis was performed in a heating rate 10 °C/min in N_2. [b] By GPC calibrated with standard polystyrene. [c] The temperature for 10% weight loss.

signals corresponding to the two different types of methyl protons at 1.70 and 2.04 ppm and the signals attributed to the two different types of olefinic protons at 6.30 and 6.86 ppm were observed. These spectra are compatible with the structure as shown in eq 3 containing *E* and *Z* forms on carbon–carbon double bonds, and this polymer structure can be confirmed to be formed by selective attack of thiyl radical to the center carbon of an allenyl group of 2, followed by abstraction of hydrogen of the thiol group by the terminal carbon of the allenyl group. The assignment of geometrical stereochemistry has been made on the basis that in the carbon–carbon double bond assigned as *Z*, the methyl and olefinic protons appear at lower field in the ^{1}H NMR according to similarity of the polymer obtained from 1 and dithiols.[4] The *E*/*Z* ratios of the double bonds in the polymer obtained from both BDT and MPS were changed from ca. 4/6 to 1/9 with reaction time, and a similar tendency was also observed in the model reaction of phenoxyallene with thiophenol.[8]

Thermal stability of the polymers obtained from 2 was compared with that of the similar molecular weight polymers obtained from 1 by using the thermogravimetric technique (Table II). The temperature for 10% weight loss of the polymer from 1 was 240–280 °C, whereas that of the polymer from 2 was more than 300 °C. This stability of the polymer from 2 may be attributed to absence of benzylic methylene groups as expected by us.

Furthermore, cross-linking of the obtained polymer, which has the reactive electron-rich carbon–carbon double bonds in the backbone, was carried out with BF_3OEt_2. To a solution of the polymer in dichloromethane was added 3 mol % of BF_3OEt_2 at room temperature to give a cross-linked polymer quantitatively in 60 s; it was slower than the cross-linking of the polymer obtained from 1 under the same conditions. Since characteristic absorptions of double bonds in the polymer at 1641 and 814 cm^{-1} disappeared almost completely in the IR spectrum of the resulting cross-linked polymer, the reactive electron-rich double bonds in the backbone of different polymer chains may undergo cationic polymerization to afford the cross-linked polymer. Further work on the polyaddition of dithiols to other diallenes as well as applications of the resulting polymers as functional materials are in progress.



(3)

Experimental Section

^{1}H NMR spectra were recorded on JEOL PMX 60SI and EX-90 spectrometers, using tetramethylsilane (TMS) as internal standard in deuteriochloroform at 27 °C. FT IR spectra were obtained with a JASCO FT/IR-3 at 25 °C. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$, number and weight average molecular weights) and its distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCP & 8000 system with a data processor, equipped with polystyrene gel columns, using tetrahydrofuran as solvent, flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

Solvents were purified by distillation according to the usual methods.

Preparation of 1,4-Bis(allenyloxy)benzene (2). A solution of 1,4-dihydroxybenzene (50 g, 0.45 mol) and propargyl bromide (12.0 g, 1 mol) in 500 mL of DMSO was added to potassium *tert*-butoxide (168 g, 1.5 mol) at room temperature. After the mixture was stirred at room temperature for 24 h, the reaction mixture was poured into a large amount of water. The solution was extracted with diethyl ether and washed with 5% ammonium chloride aqueous solution. The organic layer was dried over magnesium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (300 mesh, activated alumina) to obtain 54 g (65%) of 2: IR (neat) 1199, 1955 cm^{-1}; ^{1}H NMR (CCl_4) δ 6.87 (s, 4H), 6.70 (t, J = 6.2 Hz, 2 H), 5.43 (d, J = 6.2 Hz, 4H).

Anal. Calcd for C12H10O2: C, 77.40; H, 5.41. Found: C, 77.51; H, 5.43.

The Polyaddition of BDT or MPS to 2. Equimolar amounts of BDT or MPS and 2 were dissolved in benzene (2.5 mol/L) at 60 °C with AIBN (3 mol %) in a sealed tube under reduced pressure. After the polymers were purified by dissolution in benzene followed by precipitation in hexane, they were filtered off and dried in vacuo. Further, they were dissolved in benzene, and the solution was lyophilized. The results are summarized in Table I. IR(film) 1641, 1207, 815 cm^{-1}.

The Cross-Linking Reaction of the Polymer. To the solution of the polymer (M_n = 6400) in 2.5 mol/L of CH_2Cl_2, a catalytic amount of BF_3OEt_2 (3 mol %) was added at room temperature in CH_2Cl_2. After a stirring bar immobilized, the reaction was terminated with aqueous ammonia/MeOH. Then, the reaction mixture was poured into a large amount of CH_2Cl_2. The precipitated polymer was collected by filtration, washed several times with water, and then extracted with CH_2Cl_2 by Soxhlet extractor. The obtained polymer was dried under vacuum in desiccator: IR(KBr) 1214, 1037 cm^{-1}.

References and Notes

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